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PRECISION OF ASSESSMENT OF PALATABILITY OF FOODSTUFFS BY LABORATORY PANELS[1]

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Abstract

Two categories of quality assessment of foodstuffs by panels of judges may be distinguished. In 'grading', an absolute assessment representative of the generality of consumers is sought. In 'analysis', maximum sensitivity is desirable and emphasis is shifted from absolute to relative assessments. In four series of 'grading' tests, individual ratings were most variable in the quality region close to the lower limit of acceptability, thus increasing to about 30 the calculable size of panel required to distinguish differences of the order of 5% from an assigned standard. The threshold concentration of primary taste substances detectable varies considerably between individuals, but except in extreme cases no consistent relation between taste acuity alone and palatability judgments was indicated. However, the judging characteristics of individuals may be investigated numerically by computing the correlation coefficients and regression equations relating their assessments to the average of those of all other members of the same panels. In this way a range of sensitivity of the order of 40% was demonstrable in the tests under review, making possible an objective evaluation of the suitability of individuals for 'grading' or 'analytical' tests.

Introduction

War conditions necessitated standardization and control of the quality of a number of bulk-produced foodstuffs, resulting, in certain instances, in increased requirements for assessment of their palatability in numerical terms. It is generally agreed that such assessments must be based in the last analysis on the reactions of human judges, for as has been pointed out by Platt (8), although the *quantity* of specific attributes of taste, odour, or texture may be capable of objective measurement, their *desirability* can only be determined subjectively. On the question of the precision of subjective assessments, however, opinion diverges widely. Thus whilst Crocker (4) states that "a considerable degree of reproducibility may be obtained in organoleptic testing" and that "even persons of ordinary discrimination may become good flavour discriminators if adequately trained", Crist and Seaton (3) conclude that "the ordinary tasting-panel method, as tested by the criterion of correlation in trials by duplication, is questionable. Either its improvement or its abandonment appears to be necessary and imperative".

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Platt (8) draws a sharp distinction between assessments based on systems of scoring by a few specially trained or experienced individuals on the one hand, and direct tests of consumer preference on the other, the latter consisting of simple comparisons made by a large number of unselected people representative of the public providing the market for the product in question. Laboratory tests may themselves be subdivided in a similar manner, depending on the nature of the information sought. A commercial laboratory, for example, may wish to use a panel of tasters to grade the output of an already established product in order to prevent loss of goodwill through the sale of material deviating noticeably from the standard to which the public is accustomed. Such a panel need not comprise highly trained or expert personnel, but should consist of a small number of individuals who could be relied on to reproduce consistently the average reaction of the consuming public. What is desired here is in fact a reliable but rapid and inexpensive gauging of consumer tolerance, and excessive sensitivity would defeat this object. If on the other hand new or modified processes are being explored, laboratory palatability tests may be regarded as essentially analytical in nature. Greater sensitivity may therefore be desirable, and emphasis may be shifted from the absolute to the relative assessment of quality. Any such enhanced sensitivity must however still be in the right direction, i.e. a substance rated above-average by a panel of this type should also appeal to the general public. These considerations may be expressed in statistical terminology by stating that the taste reactions of individuals selected for laboratory panels for both grading and analytical work should be highly correlated with those of the generality of consumers. Furthermore, the average coefficient of regression of the scores assigned by individuals on the mean values resulting if all consumers made a similar test should be in the neighbourhood of unity for a grading panel. On the other hand, a high regression coefficient should be a condition of membership in an analytical panel. Clearly, the ratings of an analytical panel may always be used for grading purposes by the application of an appropriate conversion factor, but, in an institution undertaking any volume of organoleptic testing, it might be found desirable to reserve the more sensitive judges for discriminations of which the majority of the staff were incapable.

In practice, of course, perfect correlation is unattainable, but if the magnitude of the discrepancies between individuals is known, the size of panel required to produce an average assessment of specified accuracy may be calculated. A certain amount of information bearing upon this and the preceding points has accumulated from palatability tests made in these laboratories. This has accordingly been summarized and is reported below.

Analysis of Observations

Detection of Primary Tastes

Having regard to the demonstration by Blakeslee (1) and others of hereditary deficiencies in tasting ability, Knowles and Johnson (7) subjected 37 ran-

domly chosen prospective members of a palatability panel to a trial of their sensitivity to the four primary tastes, and reported the molar dilution in which each individual was able to identify the test substances used. Two men and two women failed to detect the sweet taste in the highest test concentration of sucrose, one woman could not distinguish salt from sweet, and another was unable to identify bitter. A parallel trial was subsequently undertaken in these laboratories in which similar test solutions were submitted to 56 individuals. However, whereas Knowles and Johnson's subjects comprised 19 men and 18 women, in the later Ottawa test males predominated in the ratio of 42 men to 14 women. Two of these 42 men could not detect bitter in the highest test concentration (0.05 *M* caffeine), three failed to detect the sourness of 0.003 *M* glutamic or tartaric acids, and one was unaffected by 0.05 *M* sucrose. There was no case of complete 'taste blindness' among the 14 Ottawa women, but both sexes provided instances of incorrect identification of taste stimuli. This was most pronounced in the case of tartaric acid (16 individuals), a circumstance in agreement with the observation of Knowles and Johnson (7) that "Bitter-sour indiscriminations in the low concentrations were frequent".

Both the Knowles and Johnson and Ottawa data were subjected to statistical analysis employing the probit-log dosage transformation found applicable to a wide range of physiological and psychological responses to a graded series of stimuli. As was pointed out by Bliss (2), when the results for successive concentrations are merely different observations on a single set of individuals, the percentage reacting to a specified concentration can never be less than that recorded for a lower concentration, and successive observations are strongly correlated with each other; methods of computation appropriate to this situation were originally evolved by him for the analysis of time–mortality data in toxicological studies. By this analysis it was found that in both groups of tasters the logarithms of individual threshold concentrations were approximately normally distributed. Furthermore the median thresholds, at or below which 50% of individuals reacted, computed for the two groups separately and listed in Table I, agreed closely except in the case of caffeine (bitter), for which the observed difference exceeded three times its standard error. This may reflect a real divergence in the sensitivity

TABLE I

COMPUTED MEDIAN THRESHOLD CONCENTRATIONS (MOLAR)

Trial	Sucrose (sweet)	Caffeine (bitter)	Glutamic acid (sour)	Tartaric acid (sour)	Sodium chloride (salty)
Knowles and Johnson (North Dakota)	0.0192	0.0008	0.0010	0.00026	0.0199
National Research Laboratories (Ottawa)	0.0195	0.0018	0.0008	0.00020	0.0192

of the tasters, but in view of the otherwise close agreement, the possibility of some lack of uniformity in the caffeine solutions used in the two tests cannot be excluded.

The variance of individual threshold concentrations in both groups and for all the test substances was of the same order, resulting in an average standard deviation of 0.3170 logarithmic units. In absolute units therefore, one would in general expect about 25% of all individuals to have thresholds exceeding the average in the ratio of 1.6 : 1 or more, whilst the median threshold of all persons below average in sensitivity would exceed the median of those of above-average sensitivity in the ratio of 3.3 : 1. Classification of the data from both laboratories in 2 × 2 contingency tables and calculation of the indices of association χ_c (6) listed in Table II revealed a significant degree of correlation in the sensitivity of the same individual to the sour, salt, and sweet

TABLE II

ASSOCIATION BETWEEN SENSITIVITIES TO DIFFERENT PRIMARY TASTES AS INDICATED BY χ_c FOR 2 × 2 CONTINGENCY TABLES

Test substance	Glutamic acid (sour)	Sodium chloride (salty)	Sucrose (sweet)
Caffeine (bitter)	2.16*	0.01	0.17
Glutamic acid (sour)		3.31**	3.23**
Sodium chloride (salty)			2.20*

* χ_c *attains 5% level of statistical significance.*
** χ_c *attains 1% level of statistical significance.*

test substances. Sensitivity to bitter was associated feebly with that to sour, and not at all with that to salt and sweet. In the same way, the one statistically significant value in Table III provided some suggestion that females detected glutamic acid more readily than did males, but provides no evidence of any effect of the smoking habit on taste acuity.

TABLE III

VALUES OF χ_c FOR 2 × 2 CONTINGENCY TABLE CLASSIFICATIONS OF INDIVIDUALS BY SEX AND ADDICTION TO TOBACCO, AND SENSITIVITY TO PRIMARY TASTES

Test substance	Males and females	Smokers and non-smokers
Caffeine (bitter)	0.03	1.27
Sucrose (sweet)	1.37	0.01
Glutamic acid (sour)	2.48*	0.01
Tartaric acid (sour)	1.39	0.00
Sodium chloride (salty)	1.69	0.01

* χ_c *attains 5% level of statistical significance.*

Knowles and Johnson (7) concluded that their results showed the necessity of testing the tasting ability of individuals before making selections for a panel of judges, and suggested criteria for the discrimination of "excellent", "good", and "fair" sensitivity, the last requiring the distinguishing of three of the four primary tastes in average or lower concentrations and eventual identification of the remaining taste. It must be agreed that it is difficult to imagine an individual notably deficient in sensitivity to two or more of the primary tastes functioning effectively as a judge of palatability. However, it must also be remembered that the sensation of palatability results from a combination of gustatory, olfactory, and tactile perceptions, the outcome of which is further conditioned by the subjective reaction of each individual to these various stimuli. Except in extreme cases, therefore, it would be too much to hope that this could be predicted from a single basic test.

Primary Tastes in Flavour Tests.

In order to provide some information respecting the extent to which sensitivity to the primary tastes affected judgments of flavour, a special series of samples consisting of scrambled egg containing various amounts of the foregoing test substances were made up and submitted to 30 of the 56 individuals taking part in the sensitivity determinations in the Ottawa laboratory. These special samples were tasted in sets of four, comprising an unadulterated fresh egg control and three preparations of fresh egg containing one of the test substances in an amount (calculated on a moisture basis) below, approximately equal to or definitely above the median threshold in the preceding trial. Such sets of four samples were included without identification in an extended series of flavour tests of scrambled egg made from dried egg powders, and were accordingly allotted scores by the tasters on the integral scale of 0 to 10, then used to assess the latter. In this way each of the 30 individuals participating tasted 20 special samples, of which five were controls and 15 were mixtures as described.

When analysed according to the procedure of Fisher (5), the total variance of the resulting 600 scores yielded the components shown in Table IV. These demonstrate that the average scores assigned by individual tasters to the entire series of samples varied appreciably, but that at the same time some statistically significant discrimination between the groups of samples containing different test substances, and between concentrations of these substances, was effected. The last component of variance shown in Table IV may be regarded as a measure of the basic error of tasting, namely inconsistency in the scoring of successive samples of the same material, and may be supposed to depend on acuity of perception and constancy of subjective reaction only. Relative scores allotted to samples actually differing in quality, on the other hand, involve judgment as well as perception, and consequently might be expected to exhibit more individual fluctuation. That this was not forthcoming in the present series of observations (Table IV) may have been because the differences in flavour between these test samples, although statistically demonstrable by reason of the large number of tasters

TABLE IV

ANALYSIS OF VARIANCE OF TASTERS' SCORES—FRESH EGG WITH AND WITHOUT ADDED SUBSTANCES

Source of variance	Degrees of freedom	Mean square
Between groups of samples	5	8.98**
Between samples of fresh egg	4	1.12
Between concentrations of added substances (average for all substances and tasters)	2	19.97**
Differential reaction to concentrations of individual substances (average for all tasters)	8	3.04
Between tasters (average for all samples)	29	26.56**
Differential reaction of individual tasters to groups of samples	145	1.69
Differential reaction of individual tasters to concentration of added substances	290	1.87
Differential reaction of individual tasters to samples of fresh egg	116	1.88

** *Exceeds mean square residual, 1% level of significance.*

employed, were not pronounced, and in fact corresponded to an average of less than 1 unit on the scale of assessment adopted (see Tables V and VI).

It is to be observed from Tables V and VI that, excepting one anomalous result with sucrose, the high concentration of the added substances alone was detected with any consistency, and resulted in an average reduction of palatability rating of 0.7 units. Divergence of the scores allotted to the same materials by different tasters (Table V) was however of an altogether greater order of magnitude, individuals' averages for the five control samples of fresh egg ranging from 10.0 to 5.4, and for all 20 test samples from 10.0 to 5.6. The individual (No. 10 in Table V, a male aged 39) who bestowed the maximum score on all samples indiscriminately was, as might be expected, relatively insensitive to all the primary tastes, his recorded thresholds for the test solutions exceeding the medians listed in Table I in the ratio of 4.4 for bitter, 1.3 for sweet, 2.5 for sour, and 1.6 for salty. However, taster No. 8 (a 26-year-old female) who reacted most unfavourably to the test samples, although of more than average sensitivity to sour and sweet, had an above-median threshold for bitter and was unable to identify the salty solution in the preceding trial; and, in general, correlation coefficients ranging from +0.02 (sweet) to +0.28 (bitter) were indicative of no significant association between an individual's logarithmic threshold as given by the primary test solutions and the scores subsequently allotted by him to the groups of egg samples containing the same taste substances. This finding is in agreement with the consideration, already noted, that gustatory perception is only one of several factors influencing palatability judgments.

Discrepancies between individuals' scoring of the same samples affects the reliability of palatability tests of the grading type, for in these an absolute score is required, and the panel of judges must accordingly be regarded as a theoretically random sample of the general consuming public. In self-

TABLE V

AVERAGE SCORES ALLOTTED TO GROUPS OF SAMPLES BY INDIVIDUAL TASTERS

Taster No.	Fresh egg (5 samples)	Fresh egg with addition of:					Average (20 samples)
		Sucrose (3 samples)	Caffeine (3 samples)	Glutamic acid (3 samples)	Tartaric acid (3 samples)	Sodium chloride (3 samples)	
1	7.6	8.0	7.3	8.3	7.7	7.7	7.7
2	8.0	2.3	8.0	6.7	8.0	8.3	7.0
3	8.2	8.3	8.0	7.7	7.3	8.3	8.0
4	8.8	8.7	5.3	8.0	6.7	8.3	7.5
5	9.4	8.3	10.0	9.3	9.3	10.0	9.4
6	8.8	8.3	7.7	7.7	8.0	8.7	8.3
7	10.0	8.7	10.0	10.0	10.0	9.3	9.7
8	5.6	4.7	5.7	6.7	5.0	5.7	5.6
9	8.0	7.7	8.7	7.7	7.7	7.7	7.9
10	10.0	10.0	10.0	10.0	10.0	10.0	10.0
11	7.0	6.7	7.3	6.0	7.7	7.0	7.0
12	8.2	7.7	8.3	8.7	9.0	8.3	8.4
13	7.2	4.3	4.0	6.3	7.3	7.7	6.3
14	7.6	6.0	6.7	8.0	8.0	6.0	7.1
15	10.0	8.0	10.0	9.3	8.3	10.0	9.4
16	8.0	6.0	5.0	7.3	7.7	8.3	7.2
17	7.8	8.0	7.3	7.7	7.3	7.3	7.6
18	5.4	6.3	5.7	7.3	5.3	8.3	6.1
19	8.4	6.3	8.7	6.0	7.3	8.0	7.6
20	9.4	10.0	10.0	9.7	8.7	9.7	9.6
21	6.0	7.0	5.7	6.3	5.0	6.0	6.0
22	10.0	8.7	8.7	9.3	9.7	9.3	9.4
23	8.8	7.7	8.3	8.3	8.3	9.0	8.5
24	6.8	5.0	5.3	8.3	6.3	8.7	6.8
25	9.4	8.0	7.3	7.7	8.6	7.3	8.2
26	8.8	8.3	8.3	8.7	7.3	9.3	8.5
27	8.0	7.7	8.0	7.7	8.0	7.0	7.7
28	7.0	8.0	6.7	7.3	8.0	7.3	7.4
29	6.2	7.7	6.7	7.3	6.7	7.7	7.0
30	7.4	8.3	6.3	7.7	9.0	8.0	7.7
Average	8.1	7.4	7.5	7.9	7.8	8.1	7.8

NOTE: *Necessary difference between averages of fresh egg and other groups = 0.36.*
Necessary difference between averages of other groups = 0.40.
Necessary difference between averages of individual tasters = 0.9.

contained analytical tests on the other hand, if an entire series of samples is assessed by the same judges, average differences between the ratings given by individuals to the series as a whole do not enter into comparisons of the relative scores given to specific samples. These are affected only by errors arising from sources of the type itemized in the last three lines of Table IV.

Variance of Palatability Assessments in Relation to Quality Level

It is of evident practical importance to know whether the variance of individual judgments of palatability, as expressed in numerical scores, is uniform over the range of quality encountered, and also whether some materials are productive of greater disagreement between individuals than others. Table VII summarizes the experience of this laboratory relevant to these points

TABLE VI

EFFECT OF CONCENTRATION OF ADDED SUBSTANCES ON SCORE (AVERAGE OF 30 TASTERS)

Substance	Concentration			
	Zero	Low	Medium	High
Sucrose	8.1	6.9	7.8	7.4
Caffeine	8.1	7.7	7.8	7.0
Glutamic acid	8.1	7.9	8.2	7.6
Sodium chloride	8.1	8.4	8.5	7.3
Tartaric acid	8.1	7.8	8.1	7.5
Average	8.1	7.7	8.1	7.4

NOTE: *Necessary difference between averages* = *0.3.*
Necessary difference between individual items and zero = *0.5.*
Necessary difference between individual items other than zero = *0.7.*

TABLE VII

STANDARD DEVIATION OF INDIVIDUAL ASSESSMENTS AT VARIOUS QUALITY LEVELS

Test substance	Statistic	Average score									
		10.0–9.1	9.0–8.1	8.0–7.1	7.0–6.1	6.0–5.1	5.0–4.1	4.0–3.1	3.0–2.1	2.0–1.1	1.0–0.0
Butter	Standard deviation	—	0.84	1.15	1.23	1.30	1.49	1.62	1.63	1.11	0.84
(Panel of 17)	No. of samples	—	1	45	65	52	57	30	15	11	3
Dried eggs	Standard deviation	0.59	0.83	1.14	1.38	1.66	1.66	1.54	2.17	1.97	—
(Panel of 6)	No. of samples	2	41	108	139	64	59	19	10	2	—
Dried milk	Standard deviation	—	—	0.97	1.12	1.22	1.35	1.50	1.49	—	0.59
(Panel of 14)	No. of samples	—	—	3	60	90	70	27	12	—	2
Ration biscuits	Standard deviation	—	1.10	1.25	1.36	1.61	1.76	1.84	1.56	1.98	—
(Panel of 16)	No. of samples	—	28	190	206	160	73	17	2	1	—

resulting from a fairly extensive series of palatability tests of four foodstuffs, namely ration biscuits, dried eggs, butter, and dried milk. The standard deviations shown in this table are appropriate to absolute scores, i.e., to the grading type of test, and thus include any average differences between tasters.

On the whole, the degree of variability indicated was of the same order for all four substances. Furthermore, in all four cases individual scores became clearly less consistent as quality decreased, and were possibly most discrepant in the region corresponding to scores of 2 to 5. Owing to the infrequency of samples of the lowest quality, the zone of maximum uncertainty is not well determined. The existence of such a zone in any extended series including extremely good and extremely bad samples is however implicit in the bounding of the assignable scores.

It should be noted that an increase in individual variability necessitates the employment of more judges to produce an average assessment of specified reliability. In order to equalize the variance of the scores for dried egg given in Table VII for example, nearly eight times as many judges would be required in the quality range 2 to 3 as in 8 to 9. Deductions may also be made from Table VII respecting the actual number of judges required to yield average scores of specified accuracy. Thus in order to detect, at the 5% level of statistical significance (5), samples of dried egg differing from a pre-assigned quality rating of 4.0 by 1 unit or more on the quality scale here employed, 12 judges would be needed; whilst the detection of deviations of 0.5 unit would require the averaging of 46 individual scores. Discrimination between two samples of this mediocre quality rated by different panels would call for 23 judges per sample for a necessary difference of 1 unit and for 92 per sample for a necessary difference of 0.5 unit.

Correlation of Individuals' Assessments with Panel Averages

In an introductory paragraph it was pointed out that the suitability of individuals for laboratory taste panels might be evaluated statistically in terms of regression and correlation coefficients. Ideally, such evaluations should be made by relating each individual in question to the average of the consuming public. In practice, a reasonably representative sample of the latter must suffice. Even this was not available in the present instance, but, as the panels employed in this laboratory on the tests summarized in Table VII comprised scientific workers, technicians, and members of the administrative staff unselected in respect of tasting experience, training, or ability, correlation and regression coefficients of several individuals relative to all other panel members assessing the same samples have been computed as a matter of interest, and are shown in Table VIII.

Generally speaking the highest correlation coefficients resulted from the tests of ration biscuits, and the lowest from those of dried milk. However, in fairness to the tasters employed on the latter it should be noted that the great majority of samples of these fell within a narrow range of quality (see Table VII), so that discrepancies between individuals would be expected to constitute an increased proportion of the total variance. An appreciable range is to be observed in individuals' correlation coefficients for butter (0.66 to 0.88) and dried milk (0.44 to 0.68), whilst ration biscuits gave slightly more uniform results (0.74 to 0.84). A somewhat higher degree of correlation is obviously desirable, and would operate to reduce the rather large numbers of tasters specified in the preceding section for results of statistical significance. Nevertheless this aspect of the tests was by no means wholly unsatisfactory, and certainly lends no support to the pessimistic views of Crist and Seaton (3) respecting the non-reproducibility of test panel results.

The regression coefficients listed in Table VIII, which as noted above provide a measure of the sensitivity of individuals' reactions, vary from 0.72 to 1.11 for butter, from 0.69 to 1.10 for dried milk, and from 0.68 to 1.14 for ration biscuits. For all three substances therefore, the range was of the order

TABLE VIII

CORRELATION OF INDIVIDUALS' ASSESSMENTS WITH AVERAGES OF REMAINDER OF PANEL

Test substance	Taster	No. of samples	Correlation coefficient	Regression coefficient	Average deviation of assessments from all others
Butter (Panel of 17)	*A*	130	.78	0.93	−0.26
	B	142	.88	1.09	−0.50
	C	140	.87	1.16	+0.06
	D	136	.76	0.89	−0.04
	E	127	.66	0.72	−0.54
	F	116	.81	1.11	+0.56
	G	128	.77	0.80	−0.15
	H	147	.76	0.94	−0.87
	I	117	.77	1.02	+0.06
Dried milk (Panel of 14)	*A*	307	.64	1.05	+0.52
	B	248	.54	0.95	−1.12
	J	250	.67	0.91	−0.42
	K	263	.68	1.10	−0.17
	L	296	.44	0.80	−0.45
	M	226	.54	0.86	+0.24
	N	256	.66	0.90	+0.46
	O	189	.47	0.69	+0.97
	P	222	.67	1.03	+0.46
Ration biscuits (Panel of 16)	*A*	157	.83	0.91	+0.70
	B	157	.78	1.04	−0.55
	C	139	.83	1.14	+0.09
	G	167	.75	0.68	+0.62
	J	166	.84	0.94	−0.12
	K	167	.80	0.85	−0.12
	Q	147	.74	0.96	+1.19

of 40% of the mean. The last column of Table VIII shows the amount by which the average score given by each judge exceeded or fell below the average of all other panel members assessing the same samples, and provides some further examples of consistent differences in individual preference levels of the type illustrated in Table V. The correlation coefficient, regression coefficient, and average score together provide a numerical characterization of the performance of the various judges. Taster *C* in Table VIII, for example, with a correlation coefficient of 0.87, a regression coefficient of 1.16, and an average preference level differing by only +0.06 from the remainder of the panel would be an obvious choice for the analytical assessment of butter, whilst *E*, with a correlation coefficient of 0.66, a regression coefficient of 0.72, and a mean deviation from the average preference of −0.54 scale units, equally obviously would not. Taster *C* also had the highest regression coefficient of those members of the ration biscuit panel investigated. Taster *B* had regression coefficients in excess of unity for both butter and ration biscuits but also exhibited a mean deviation from the average preference level of about −0.5 units in both instances, again illustrating the necessity of maintaining panel personnel unchanged throughout any series of samples for which maximum precision of relative assessment is desired.

Conclusions

The results described above may be summarized as follows:

There is appreciable variation in the ability to detect primary taste substances, the logarithms of individual threshold concentrations being approximately normally distributed. However, assessments of the palatability of foodstuffs depend upon olfactory and tactile as well as upon gustatory sensations, and are further conditioned by the subjective reaction of individuals to these stimuli. Except in extreme cases therefore, no consistent relation between taste acuity alone and palatability judgments is to be anticipated.

Two categories of quality assessment of foodstuffs by panels of judges may be distinguished. In the 'grading' type of test an absolute assessment is sought, and the panel must provide a representative sample of the reaction of the generality of consumers to the product in question. In tests of the 'analytical' type the effects of new or modified processes are compared, maximum sensitivity is desirable, and emphasis is shifted from absolute to relative assessments.

Analogous considerations apply to the fluctuations affecting the reproducibility of assessments, and a distinction may be made between consistent differences in preference level on the one hand, and the differential reaction of individual judges to particular samples on the other. Providing an entire series of samples is assessed by the same judges, the former may be eliminated from comparisons made within a test of the 'analytical' type. They cannot however be excluded from assessments on an absolute scale, in which they must be expected to constitute a major source of error.

In a series of tests in this laboratory in which quality was assessed on a numerical scale of 0 to 10, individual ratings became progressively more erratic as quality deteriorated, and were judged to reach a maximum of variability in the quality region corresponding to average scores of 2 to 5. This circumstance has the effect of increasing considerably the size of panel required to produce results of statistical significance when grading products of a quality close to the lower limit of acceptability.

The assessment characteristics of individuals may be investigated numerically by calculation of the coefficients of correlation and regression relating their scores to the average of those of all other members of the panel, and also by determining the mean amount by which their preferences are in excess or defect of the remaining panel average. In the tests considered here there was appreciable variation in both the correlation and regression coefficients of individuals, the latter indicating a range of sensitivity of the order of 40% of the mean. By statistics such as these the suitability of individuals for grading or analytical panels may be objectively evaluated, although in the case of grading panels it must always be borne in mind that the aim is to produce assessments characteristic of the consuming public in general rather than of the laboratory staff in particular.

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DRIED WHOLE EGG POWDER

XX. THE EFFECT OF GRADE OF EGGS, LOCALITY AND MONTH OF PRODUCTION, AND CLIMATIC CONDITIONS ON THE SOLIDS CONTENT OF LIQUID EGG AND ON THE QUALITY OF THE POWDER PRODUCED[1]

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Abstract

Grade *A* large eggs had the lowest average solids content (25.6%) of the grades studied and Grade *C* eggs had the highest (26.6%). The solids content increased during the period from December 1944 to July 1945. The total increase during this interval was about 0.5%.

The average potassium chloride value of powder produced from Grades *B* and *C* eggs was higher than the value for Grade *A* medium eggs; Grade *A* medium and pullet eggs produced powder better in this quality attribute than Grade *A* large (differences of about 2%). The use of Grade *C* eggs resulted in a powder with an average fluorescence value about 2 units greater than for powder from any other grade of eggs. The month of egg production affected quality measures on the resulting powder. As the season progressed there was a decrease in the fluorescence value and pH and an increase in potassium chloride value and foaming volume value.

The changes noted could not be attributed to climatic conditions, but may be attributable to feeding practices and to increased age of the hen.

Introduction

The increased production of dried eggs in Canada has focused attention on possible differences between lots of eggs that may affect both the yield and quality of the resulting powder. Recurring statements from some producers of powder indicated that eggs from different parts of the country varied widely in solids content. One processor claimed that eggs from one area consistently produced 4% less powder than eggs from another area. Therefore, it seemed advisable to attempt a monthly assessment of the solids content of various grades of eggs from different parts of the country.

There is some evidence that eggs produced between November and March are of the highest quality (3, 4, 5, 7, 12). Although these reports did not deal with solids content specifically, they describe decreases in quality from March to November as assessed by the condition of the thick white, the percentage of thick white, yolk index (4, 5), and candling appearance (7). There was no seasonal change in yolk colour (4, 5) but this may be attributed to the use of standard mash for feeding the experimental birds. One Canadian report indicates that the albumin index of eggs produced in March is higher than that of eggs produced in June (3).

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Therefore, simultaneously with an assessment of solids content of the liquid eggs, some of the material was dried and the yield determined. The properties of the powder were assessed, using the quality tests currently applied to dried egg powder (6) and a test of baking properties (9). The colour of the powder was measured on a colour comparator (13). The present paper describes differences in solids content of the liquid eggs, and in yield and quality of the dried product. The colour measurements will be discussed as part of a subsequent paper on the colour of dried egg powder (10).

Materials and Methods

The original experimental design required the shipment of eggs from Vancouver, Edmonton, Winnipeg, London, Belleville, and Three Rivers. While these did not represent all the areas from which eggs are purchased for drying, they did represent the areas subject to controversy and were believed to be a good cross-section of Canada's egg producing districts. Since surplus eggs become available in Canada in December and production falls off the following July when the hens begin to moult, eggs were taken from current receipts on the 15th of each month from December 1944 to July 1945. This would represent the eggs most likely to be dried. Five dozen of each of the following grades were to be shipped at each sampling time: *A* large, *A* medium, *A* pullet, *B* and *C*. Since Canadian eggs can be classed as *B* and *C* for dirty shells as well as for quality (2), the samples representing these grades were selected on the basis of quality only. All eggs were to be drawn from current receipts in the areas designated, and samples were taken and graded by inspectors of the Special Products Board of the Canadian Department of Agriculture.

Unfortunately, the original plan could not be adhered to entirely. Only four areas could supply eggs in December 1944, and it was impossible to obtain the required *B* and *C* eggs from the Vancouver area. From time to time, single items were missing in the various consignments. Nevertheless, it was believed that the survey was sufficiently complete to permit conclusions of value. Altogether, 224 five-dozen lots of eggs were used in the study.

Upon receipt in the laboratory, the eggs of each of the various grades were broken and mixed; samples were then drawn for determinations of solids content (1, p. 308) and the remainder was weighed before going to the laboratory spray drier (14) for dehydration (drying temperatures: inlet, 250° F.; outlet, 140° F.). After dehydration the material from the main chamber and the secondary collector were weighed separately, and the moisture contents determined (11). From these values, the recovered solids were calculated as a percentage of the solids introduced into the drier.

Only the powder from the main chamber was used for measurement of fluorescence value (8), potassium chloride value (11), pH (6), and foaming volume (9).

Results

The significance of the results was assessed by analyses of variance. Two comparisons were made: the first compared Grade *A* eggs of all sizes from the six areas for the months of January to July 1945; the second compared Grade *A* medium eggs with Grades *B* and *C* eggs for the same collection times but for five areas only. Since the mathematical treatment showed little evidence of differential behaviour, the presentation of the results has been simplified by the use of tables of means and necessary differences (Tables I, II, and III). The effect of area of production on solids content of Grade *A* eggs almost attained significance and was given further consideration (Table IV). There appeared to be some relation between quality and time of production and possibly some relation between quality and climatic conditions, shown by tables of correlation coefficients (Tables V and VI).

Solids Content and Yield

The results indicated that Grade *A* large eggs had a significantly lower solids content than Grade *A* medium and Grade *A* pullet eggs, while Grade *C* eggs had the greatest solids content (Table I). Area of production had a significant effect on the solids content of Grades *B* and *C* eggs and the effect almost attained significance for Grade *A* eggs (Table II). Although the differences are small, there is generally a tendency for solids content to increase as the season progresses (Table III). This would correspond to a previously observed seasonal trend in loss of quality before the candling lamp (7). One particular feature is increase in the size of the air cell that is believed to accompany loss of moisture through the shell.

TABLE I

RELATION BETWEEN GRADE OF EGGS, SOLIDS CONTENT, AND QUALITY OF EGG POWDER PRODUCED DURING A SEVEN MONTH PERIOD

Grade of eggs	Solids content, %	Quality of powder			
		Fluorescence value	Potassium chloride value, %	pH	Foaming volume, ml.
Averages for eggs produced in six areas					
A large	25.6	23.1	65.8	8.76	235
A medium	25.9	21.3	66.6	8.75	247
A pullet	25.9	21.8	68.0	8.67	241
Necessary difference, 5% level	0.3	1.6[1]	1.8	0.09[1]	24[1]
Averages for eggs produced in five areas					
A medium	26.0	21.3	67.0	8.73	247
B	26.2	22.4	69.5	8.67	247
C	26.6	24.6	69.7	8.59	243
Necessary difference, 5% level	0.3	1.4	1.7	0.13[1]	20[1]

[1] *Difference not significant.*

TABLE II

RELATION BETWEEN AREA IN WHICH EGGS ARE PRODUCED, SOLIDS CONTENT, AND QUALITY OF EGG POWDER PRODUCED DURING A SEVEN MONTH PERIOD

Area of production	Solids content, %	Quality of powder			
		Fluorescence value	Potassium chloride value, %	pH	Foaming volume, ml.
Averages for Grade A eggs					
Vancouver	25.7	23.3	64.9	8.75	242
Edmonton	25.6	21.4	68.5	8.74	252
Winnipeg	25.5	22.4	66.2	8.78	242
London	25.7	22.5	66.7	8.73	239
Belleville	25.8	20.4	68.2	8.74	250
Three Rivers	26.0	21.9	65.4	8.67	236
Necessary difference, 5% level	0.4[1]	2.2[1]	2.6	0.13[1]	33[1]
Averages for Grades A medium, B, and C eggs					
Edmonton	26.7	23.4	70.8	8.60	249
Winnipeg	26.0	22.8	67.5	8.78	253
London	26.1	21.9	69.3	8.70	238
Belleville	25.8	21.3	67.5	8.66	251
Three Rivers	26.5	23.8	67.8	8.59	238
Necessary difference, 5% level	0.4	1.9[1]	2.2	0.17[1]	25[1]

[1] *Difference not significant.*

The effect of area of production on the solids content was given further consideration (Table IV). This table indicates a greater proportion of eggs of low solids content from Western Canada. However, Grade *C* eggs from Edmonton had high solids contents (average, 27.8%), thus accounting for the high value noted in the second part of Table II.

The only differential behaviour of significance was noted for eggs from Belleville. Grade *C* eggs from this area had, on the average, lower solids content than Grade *B* eggs, which in turn had a lower solids than Grade *A* mediums. The average values were: Grade *C*, 25.5%; Grade *B*, 25.8%; Grade *A* medium, 26.0%. No explanation can be offered to show why these results do not conform to other data presented in this paper or to everyday experience.

Calculations on powder yield in relation to solids entering the drier showed no differences in drying characteristics as a result of differences in grade, area, or time of production. The average recovery on the model drier was 92%. Although the distribution curve was slightly skewed, the standard deviation was calculated as 6%, which gives some indication of the variability observed.

TABLE III

RELATION BETWEEN MONTH IN WHICH EGGS ARE PRODUCED, SOLIDS CONTENT, AND QUALITY OF THE POWDER PRODUCED

Month of production, 1944–5	Solids content, %	Quality of the powder			
		Fluorescence value	Potassium chloride value, %	pH	Foaming volume, ml.
Averages for Grade A eggs produced in six areas					
December[1]	25.4	21.9	61.2	8.96	223
January	25.6	24.0	64.0	8.88	234
February	25.6	24.8	66.4	8.74	219
March	25.7	21.5	69.3	8.73	265
April	25.9	22.5	65.9	8.74	237
May	25.8	21.8	65.6	8.76	232
June	26.2	21.6	71.7	8.78	285
July	26.0	17.9	66.7	8.51	235
Necessary difference, 5% level	0.5	2.4	2.8	0.14	36
Averages for Grades A medium, B, and C eggs produced in five areas					
December[1]	26.2	22.3	61.6	8.88	223
January	26.2	24.9	64.9	8.80	234
February	26.2	26.1	66.1	8.66	220
March	26.1	20.6	69.0	8.72	251
April	26.2	22.1	69.8	8.77	248
May	26.3	22.9	69.3	8.70	244
June	26.5	22.3	72.7	8.73	282
July	26.5	19.4	68.3	8.26	239
Necessary difference, 5% level	0.4	2.2	2.6	0.20	30

[1] *Eggs from only four areas available in December. Therefore these measurements not included in analysis of variance.*

TABLE IV

VARIATION IN SOLIDS CONTENT OF VARIOUS GRADES OF EGGS FROM VARIOUS DISTRICTS SAMPLED DURING AN EIGHT MONTH PERIOD

Grade of eggs	Solids content, %			Area and number of samples greater or less than standard deviation											
				Greater						Less					
	Mean	S.d.	Range	*V.*	*E.*	*W.*	*L.*	*B.*	*T.R.*	*V.*	*E.*	*W.*	*L.*	*B.*	*T.R.*
Production from six areas															
Grade *A* large	25.6	0.5	24.5 – 26.3	1	1	1	1	0	3	1	3	1	1	1	0
Grade *A* medium and pullet	25.9	0.5	24.6 – 27.3	0	1	0	2	1	3	5	1	0	3	1	0
Production from five areas															
Grade *B*	26.2	0.4	25.0 – 27.5	—	0	1	0	1	0	—	2	0	0	0	1
Grade *C*	26.7	1.0	25.5 – 29.9	—	2	0	0	0	0	—	0	0	0	2	0

The data in Table IV indicated that, in spite of fairly constant behaviour during the drying operation, variation in production is possible because of differences in solids content of the eggs. In Canada, only eggs of *B* grade or better are dried, thereby making possible variation in recovered solids of between 24.5 and 27.5 lb. per 100 lb. of liquid egg introduced into the drier. Since the quantity of liquid egg dried in one day in a commercial plant greatly exceeds the size of the samples studied here, some reduction in this variation is likely. If variations of the magnitude of the standard deviations (Grades *A* and *B* eggs, Table IV) are encountered in commercial practice, 100 lb. melange may produce between 25.1 and 26.6 lb. of powder. That is, a plant drying 40,000 lb. of liquid egg per day may recover between 10,040 and 10,640 lb. of solids. These values are more extreme than, but support, the 400 lb. differences reported from some commercial plants producing about this quantity of powder.

Quality of the Powder Produced

Neither grade of eggs nor area of production had a significant effect on the pH and foaming volume values of the powder produced, but month of production appeared to affect all quality measures (Tables I, II, and III). The use of Grade *C* eggs resulted in powders with increased fluorescence values. The high fluorescence value noted for Grade *A* large eggs was attributable to the high values for this grade of eggs from the Vancouver area. Powders produced from Grade *A* pullet eggs had higher potassium chloride values than powder from Grade *A* large eggs, and Grades *B* and *C* eggs produced powder significantly better in this quality attribute than Grade *A* mediums. Powder from Grade *A* eggs from Edmonton and Belleville areas had higher potassium chloride values than powder from similar eggs produced in the Vancouver and Three Rivers areas. The comparison of *B* and *C* with *A* medium eggs further supported the high potassium chloride values for eggs from the Edmonton area.

Time of production affected all quality attributes of the powder (Table III). Fluorescence values were high in February and decreased thereafter, while potassium chloride values progressively increased until June and decreased markedly in July (time of first moult). A regular decrease in pH was observed throughout the period studied. Foaming volume values were greatest in March and June. Since there were changes in quality with month of production, which may have been the results of climatic conditions, these changes were studied further by calculation of the correlation coefficients between quality attributes and climatic condition.

Correlations Between Time, Climatic Conditions, and Quality

Correlation of the various measurements for Grade *A* eggs or powder from Grade *A* eggs with time of production is shown in Table V. Average values for solids content and potassium chloride value and foaming value of the powder increased as the season of production progressed, while average fluorescence value and pH of the powder decreased. The only relations

attaining significance were those between time of production and solids content, and time of production and pH. Considered independently of time effects, positive correlations were observed between average solids content and average fluorescence, potassium chloride and pH values of the powder. However, these relations failed to attain significance.

TABLE V

CORRELATION COEFFICIENTS BETWEEN TIME OF PRODUCTION, AVERAGE SOLIDS CONTENT OF LIQUID EGG, AND AVERAGE VALUES FOR QUALITY MEASUREMENTS ON EGG POWDER

Items correlated	Correlation coefficient
Time correlated with averages for: (6 degrees of freedom)	
Solids content of liquid eggs	.886**
Fluorescence value of powder	−.704*
Potassium chloride value of powder	.656
pH of reconstituted powder	−.799*
Foaming volume for powder	.456
Correlation of solids content with averages for quality measures independent of time effects: (5 degrees of freedom)	
Fluorescence value of powder	.417
Potassium chloride value of powder	.558
pH of reconstituted powder	.375
Foaming volume for powder	.077

* *5% point of statistical significance,* $r = \pm .707$.
** *1% point of statistical significance,* $r = \pm .834$.

When considering the effects of climatic conditions (dry bulb temperature, sunshine, rainfall) it was believed that the average condition occurring during the first 15 days of the month might be correlated with the various measures, if the quality was affected by the climate to which the egg is exposed just after laying. Conversely, if climate were affecting egg quality prior to laying, the average condition occurring during the last 15 days of the preceding month might be correlated with the measures. To make the comparison, correlation coefficients were calculated independently of time and area. Only one relation attained significance (5% level) and since there were 30 comparisons this might be expected to occur by chance (Table VI). It was thought possible that significant relations might be observed if the data were broken down for periods from January to March and April to June, i.e., for periods when hens are sheltered or outside. However, even with this breakdown none of the coefficients became significant.

In general, the failure of the correlations to attain significance for any factor other than time indicates that the age of the hen may be the most important single factor responsible for the changes noted in the solids content

TABLE VI

CORRELATION COEFFICIENTS RELATING CLIMATIC CONDITIONS TO THE AVERAGE SOLIDS CONTENT OF GRADE *A* EGGS COLLECTED ON THE 15TH OF EACH MONTH FROM JANUARY TO JUNE AND TO THE QUALITY OF THE POWDER PRODUCED (INDEPENDENT OF TIME AND AREA[1])

Average condition during the first 15 days of the months correlated with:	Correlation coefficient (15 degrees of freedom)		
	Dry bulb temperature	Sunshine	Rainfall
Liquid egg			
Solids content	−.313	−.160	.354
Powdered egg			
Fluorescence value	.068	−.411	.196
Potassium chloride value	.195	.439	.360
pH	−.143	.280	.096
Foaming volume	.259	−.483*	−.072
Average condition during the last 15 days of the preceding months correlated with:			
Liquid egg			
Solids content	.187	−.145	.282
Powdered egg			
Fluorescence value	.008	−.345	.373
Potassium chloride value	−.030	−.353	.336
pH	−.021	.147	−.040
Foaming volume	−.045	−.306	−.255

[1]*Only samples taken from January to June and eggs from Three Rivers, Winnipeg, Edmonton, and Vancouver were considered in this treatment.*

* *5% point of statistical significance,* $r = \pm .482$.

of the liquid egg and in the quality of the powder produced. The differences noted for various areas may be attributable to local variations in feeding practice.

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THE APPLICATION OF DUST-LAYING OIL TO WOOL[1]

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Abstract

A process is described for the application of dust-laying oil to woollen blankets, in which use is made of a positively charged oil-in-water emulsion. During a commercial-scale trial of this process, difficulty was encountered in the form of a progressive build-up of oil and fatty acid after repeated laundering and oiling. The inclusion in the laundering formula of modified soda in a soap : soda ratio of 3 : 1 has been found to give satisfactory control of the fatty acid content, and to assist greatly in preventing the accumulation of oil.

Introduction

The treatment of hospital bed-clothes with dust-laying oil has been shown to result in a marked reduction in the number of bacteria distributed into the air during bed-making (3). Of the several methods available for the application of oil to wool, the most satisfactory is that developed by Harwood, Powney, and Edwards (2) in which use is made of a dilute oil-in-water emulsion stabilized by a cation-active emulsifying agent. The chemical aspects of this process have been investigated by Bayley and Weatherburn (1) and a somewhat modified procedure has been proposed.

The present paper deals first with a practical trial of this process on a commercial scale. During the course of this trial difficulty was encountered in the form of an objectionable accumulation of oil and fatty acid on the wool after repeated laundering and oiling. The remainder of the paper deals with a method for overcoming this difficulty.

Experimental

The procedure, as outlined in the previous paper (1), comprises a preliminary laundering, consisting of two suds with soap, two rinses with water, and souring at pH 5.0 with sodium silicofluoride. This is followed by the oiling operation in which a stock oil emulsion is added in sufficient quantity to give the desired degree of oiling on the wool.

Preparation of Stock Emulsion

For the sake of convenience in shipping and storage, stock emulsions containing as high a percentage of oil as possible are desirable. Emulsions containing 70% of oil and 1.75% of a commercial preparation of cetyldimethylbenzylammonium chloride have been prepared and found satisfactory. Emulsions containing higher proportions of the emulsifying agent are equally stable, but an excess should be avoided, both from the standpoint of economy

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and because of the retarding effect on the rate of exhaustion of the treating bath (1).

The stock emulsion was prepared as follows:

Oil*	70% by weight
Emulsifying agent†	1.75% by weight
Water (140° to 160° F.)	28.25% by weight

The emulsifying agent was dissolved in the hot water, the oil was stirred in, and the mixture was passed through a colloid mill. This emulsion tended to "cream" on standing, i.e., to separate into two layers, the upper one of which contained a high proportion of the oil, whereas the lower one was largely water. There was no separation of clear oil, however, and, on gentle mixing, an emulsion of uniform appearance was again obtained.

The emulsion did not freeze on storage for 96 hr. at 30° F., and on being restored to room temperature, appeared to be unchanged. After storage for a similar length of time at 0° F., however, the emulsion solidified, and on subsequent melting it broke down with the separation of clear oil. Metal containers in which the emulsion was stored were found to be rusted after a short time. It is therefore necessary to use non-rusting containers, and to avoid freezing of the emulsion.

Method of Oiling

A full-scale trial was carried out in commercial laundry equipment at the Sanitary Laundry, Ottawa. This trial involved the laundering and oiling of 200 woollen blankets, divided into three batches, *A*, *B*, and *C*, containing 67, 67, and 66 blankets, respectively. Batches *A* and *B* were laundered and oiled once, while Batch *C* was given three additional treatments, making a total of four launderings and oilings for this batch.

A piece of the woollen blanket material measuring 12 by 12 in. was pinned to each of six test blankets in each load, and the loads were laundered and oiled according to the following formula:

Operation	Material	Time, min.
1. Suds	Soap	10
2. Suds	Soap	10
3. Rinse	Water	5
4. Rinse	Water	5
5. Sour	Sodium silicofluoride	5 – 10
6. Oiling	Stock emulsion	10

The water level was maintained at the rinse level, and the temperature at 100 to 110° F. during each operation. Softened water was used throughout. Dry powdered low-titre soap was added to the wheel in sufficient quantity to give a good suds.

* *Marcol HX, supplied by Imperial Oil Company.*

† *Triton K–60, supplied by Rohm and Haas Company.*

In the souring operation, dry sodium silicofluoride was added in small quantities until the pH was reduced to 5.0. For the first two loads the time of souring was five minutes. It was apparent that the souring was not complete in these loads, since the liquor in the washer at the end of operation 5 was opalescent, indicating the presence of soap, and the oil was not completely exhausted from the bath in operation 6. Accordingly, in the succeeding loads both the quantity of sour and the time of treatment were increased. Details of the souring conditions are given in Table I. It was found that approximately 1 lb. of sodium silicofluoride per 100 lb. of load and 10 min. treatment were required to ensure complete souring. The term "complete souring" may be defined as the reduction of the soap content of the blanket to an amount equivalent to, or less than, the amount of emulsifying agent added in the stock emulsion in operation 6. It has been shown (1) that under these conditions the presence of soap does not interfere with the oiling process.

TABLE I

SOURING DATA

Batch	Load No.	Weight sour per 100 lb. load, lb.	Time, min.	pH of souring liquor	Appearance of souring liquor and residual oil bath
A	1	0.30	5	5.1	Cloudy
B	2	0.37	5	4.9	Cloudy
C	3	0.90	10	5.5	Faintly cloudy
C	4	1.00	10	5.1	Clear
C	5	1.00	10	4.5	Clear
C	6	1.00	10	4.4	Clear

For the sake of convenience in measuring, the stock emulsion was diluted to a concentration of 3.85 lb. oil per gal. (132 lb. diluted to 24 gal.). Four gallons of this material was added to each load. Since the average load weight was 300 lb. the estimated oil content of the treated blankets was:

$$\frac{3.85 \times 4 \times 100}{300 + (3.85 \times 4)} = 4.9\%$$

After oiling, the blankets were hydro-extracted and dried at room temperature by hanging. Four samples for analysis were cut from the body of each test blanket, and two samples from each pinned-on test-piece.

Determination of Oil and Fatty Acid Content of Oiled Blankets

The samples were conditioned for 24 hr. at 70° F. and 65% relative humidity. A 10 to 15 gm. sample (weighed accurately) was extracted for three hours with 150 ml. of petroleum ether (boiling range 30 to 60° C.) in a Soxhlet apparatus. The ether extract was filtered into a second flask, and the first flask and filter paper were washed out with a further 25 ml. portion of petroleum ether. The excess ether was distilled from the combined extract and washings, the

residue was transferred to a weighed evaporating dish, and the flask was washed out with petroleum ether, the washings being added to the dish. The remaining ether was evaporated off on a boiling water-bath, and the heating continued for 20 min. The evaporating dish was cooled in a desiccator for 15 min. and weighed.

After weighing, the extract was dissolved in 25 ml. of 95% ethyl alcohol and titrated with $N/10$ sodium hydroxide solution, using phenolphthalein indicator. The blank on 25 ml. of the alcohol was determined and subtracted from the titration value. The weight of fatty acid, calculated as stearic, was estimated and subtracted from the total weight of extracted matter to give the weight of oil recovered.

The results of these analyses are summarized in Table II. The standard deviations were calculated in the usual manner, viz.:

$$S.D. = \sqrt{\frac{\Sigma X^2}{N} - \bar{X}^2},$$

where X = the result of a single determination,

$\bar{X}$ = the mean for N determinations,

N = the number of determinations.

In Table II, the *B* samples were taken from the body of the test blankets. Each figure is an average of 24 determinations. The *T.P.* samples were taken from the pinned-on test-pieces. Each figure is an average of 12 determinations.

TABLE II

OIL AND FATTY ACID ANALYSIS OF OILED WOOL BLANKETS

Batch	Load No.	No. of oilings	Oil content, %				Fatty acid content, %			
			B samples		*T.P.* samples		*B* samples		*T.P.* samples	
			Av.	Standard deviation	Av.	Standard deviation	Av.	Standard deviation	Av.	Standard deviation
A	1	1	4.0	2.97	4.6	2.96	0.22	0.156	0.18	0.116
B	2	1	3.2	2.61	7.2	2.35	0.20	0.095	0.21	0.083
C	3	1	4.2	2.85	4.7	2.15	0.44	0.262	0.52	0.226
C	4	2	7.5	2.79	7.0	3.03	1.15	0.239	1.09	0.187
C	5	3	9.2	1.88	9.4	1.68	1.59	0.319	1.72	0.455
C	6	4	9.4	1.54	8.6	0.38	2.36	0.526	2.01	0.393

Discussion of Table II

The distribution of oil throughout the load is in general quite variable, particularly on the first oiling (loads 1, 2, and 3). There appears to be a tendency toward more uniform oiling, indicated by a decrease in the standard deviation, in loads 4, 5, and 6. This may be partially due to the levelling effect of repeated laundering and oiling, i.e., the repeated laundering tends to remove oil from the "high" areas, and the repeated oiling tends to fill in

the "low" areas. The greater uniformity of loads 4, 5, and 6 may also be partially explained by the fact that more complete souring was obtained in these loads. On the first addition of sour, the pH falls rapidly and then rises gradually as reaction with the soap adsorbed by the wool takes place. It is therefore necessary not only to use sufficient sour to hydrolyse all the soap present, but also to allow sufficient time for completion of the reaction. It is obvious that five minutes is not a sufficiently long souring time when dry sodium silicofluoride is used, since 0.37 lb. of sour per 100 lb. load reduced the pH to 4.9 in five minutes (load 2), whereas 0.90 lb. reduced the pH to only 5.5 after 10 min. (load 3).

The completeness of souring may be judged from the appearance of the souring liquor remaining in the washer at the end of operation 5, and of the residual oil bath remaining in the washer at the end of operation 6, both of which should be perfectly clear. On this basis it was concluded that souring was incomplete in loads 1 and 2, almost complete in load 3, and complete in the remaining loads.

When soap is destroyed by sour, free fatty acid is liberated and is deposited on the wool. The fatty acid content of the wool should, therefore, give some indication of the efficiency of the souring operation. There was considerably less deposition of fatty acid in the first two loads than in load 3; this confirmed the above conclusion. The increasing amounts of fatty acid observed in loads 4, 5, and 6 are due to the action of sour remaining in the wool from the previous laundering. This will be discussed more fully in a later section.

It would appear from the data given that the oil content levels off at 9 to 10%, but later work has shown that, with repeated oilings, the oil content may build up to 13 to 14% (see Table IV). The fatty acid content also builds up progressively and after four launderings and oilings shows no evidence of levelling off.

A fair degree of correlation was found between the oil content of the blankets and that of the pinned-on test-pieces. Such test-pieces could, therefore, be used to give an indication of the degree of oiling obtained on the load. It should be pointed out, however, that the analysis of a test-piece gives only the amount of oil picked up during the current oiling, and gives no indication of the amount of oil that may remain in the wool from previous oilings. The usefulness of test-pieces is thus limited unless the residual oil content can be reduced to a constant value after each laundering. This will be discussed further in the next section.

At this stage of the investigation, it was concluded that the process is satisfactory in so far as the oiling of previously unoiled wool is concerned, but that on repeated oilings there is an objectionable accumulation of both oil and fatty acid. Further work was therefore directed toward the correction of these disadvantages.

Control of Fatty Acid Content

The cause of the build up of fatty acid was investigated in the following manner. Two samples of wool were prepared: Sample *A* was taken from blankets that had been previously oiled four times, and was extracted with petroleum ether. This treatment removed oil and fatty acid, but did not remove sodium silicofluoride. Sample *B* was taken from new blankets, and was also extracted with petroleum ether. These samples were laundered with 0.3% soap solution at 100° F., rinsed in water, dried, and the fatty acid content was determined (Table III).

TABLE III

FATTY ACID CONTENT OF LAUNDERED WOOL

Sample	Fatty acid, %
A—Previously oiled wool	1.85
B—New wool	0.05

From these results it is apparent that sodium silicofluoride remaining in the wool from previous launderings causes excessive hydrolysis of soap during subsequent laundering, and is thus responsible for the high fatty acid content.

It was believed that the inclusion of an alkaline builder in the laundering formula would neutralize the excess acidity of the wool due to the presence of sour, and thus prevent further decomposition of soap. The alkali should also react with any fatty acid already deposited on the wool, so that at the conclusion of the treatment, the only fatty acid present would be that due to the decomposition of the small amount of soap left in the wool after rinsing.

Since strong alkalies have an injurious effect on wool, it was necessary to select one that would not raise appreciably the pH of the soap solution. Of the alkalies commonly used in laundering, sodium sesquicarbonate ("modified soda") was found to be most satisfactory in this respect.

Pilot Plant Trial

A pilot plant trial was carried out, using a 24 by 24 in. monel laundry wash wheel. Loads 7, 8, and 9 were made up of blankets that had been previously oiled four times, while load 10 was composed of new blankets.

Each load weighed approximately 15 lb. and was laundered according to the following formula:

Operation	Materials	Time, min.
1. Suds	Soap + modified soda	10
2. Suds	Soap + modified soda	10
3. Rinse	Water	5
4. Rinse	Water	5
5. Sour	Sodium silicofluoride	10
6. Oiling	Stock emulsion	10

The water level was maintained at the rinse level, and the temperature at 100 to 110° F. during each operation.

The water used was unsoftened Ottawa city tap water having a hardness of 4.5 to 5.0 grains of calcium carbonate per Imperial gallon. Soap flakes were used in an amount equal to 2.2% of the weight of the load. The modified soda was a mixture of 55.8% sodium carbonate and 44.2% sodium bicarbonate. The soap : soda ratio is indicated in Table IV. Dry sodium silicofluoride was added in an amount equal to 1% of the weight of the load. The stock emulsion was prepared as previously described and the volume estimated to give 5% oil on the wool was used.

At the conclusion of the oiling operation the blankets were hydro-extracted and dried at room temperature by hanging. Three consecutive launderings and oilings were given. In all of these trials complete exhaustion of the oil bath was obtained.

Samples of the oiled blankets were taken for analysis and in some cases samples were also removed immediately prior to oiling (between operations 5 and 6). The oil and fatty acid content of the samples are given in Table IV, in which each figure is an average of six determinations.

TABLE IV

EFFECT OF SOAP : ALKALI RATIO ON OIL AND FATTY ACID CONTENT OF OILED WOOL BLANKETS

Load No.	7		8		9		10	
Previous history	4 launderings and oilings		4 launderings and oilings		4 launderings and oilings		New blankets	
Ratio soap : mod. soda	5 : 1		3 : 1		1 : 1		3 : 1	
Number of launderings or oilings	Oil, %	Fatty acid, %	Oil, %	Fatty acid, %	Oil, %	Fatty acid, %	Oil, %	Fatty acid, %
Controls	10.2	1.84	10.2	1.84	10.2	1.84	0.1	0.01
1st laundering	—	—	—	—	7.8	1.54	—	—
1st oiling	12.3	3.13	12.5	3.18	10.1	1.44	4.4	0.67
2nd laundering	—	—	—	—	3.6	0.43	1.4	0.54
2nd oiling	13.4	3.78	12.0	3.51	9.1	0.38	4.8	0.49
3rd laundering	—	—	—	—	5.6	0.38	—	—
3rd oiling	13.6	4.06	12.8	3.11	10.8	0.39	5.7	0.37

Discussion

From the data presented it is apparent that, in the processing of previously unoiled blankets, the inclusion in the laundering formula of soap and modified soda in a 3 : 1 ratio maintains the fatty acid content of the wool at a satisfactory level. If, however, the fatty acid content has been allowed to build up (e.g., from the use of insufficient modified soda in previous laundering), it is necessary to increase the proportion of modified soda for several launderings in order to reduce the fatty acid to the desired level.

The inclusion of modified soda also assists in the removal of oil from the wool during the laundering process, and hence tends to prevent too great a build-up of oil on the treated blankets. Harwood, Powney, and Edwards (2) have suggested that the oil content should not greatly exceed 7%. Although the data are somewhat limited, it would appear that the proposed procedure would meet this requirement satisfactorily.

One analytical figure (1.4%) was obtained for the residual oil content after laundering. It may be inferred, however, from the oil content of the treated blankets that the residual oil is reduced to 1 to 2% after each laundering. It would therefore be possible to use test-pieces to give an approximate estimation of the oil content. If the process is carried out carefully, however, there would seem to be little need for analytical control. As long as complete exhaustion of the oil bath is obtained as judged visually, it is certain that the wool will contain sufficient oil, and an excess can readily be detected by the slightly greasy feel that becomes apparent when the oil content exceeds 8 to 9%.

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AN AIR-BASE STEREOSCOPE[1]

By R. H. Field[2]

Abstract

Three magnifying stereoscopes, intended for orienting stereo pairs of vertical air photographs and then ruling in the directions of the projections of the air bases on the photographs, were designed and constructed in the National Research Laboratories for the Department of Mines and Resources. Some features found useful in previously designed photogrammetric instruments were incorporated.

Introduction

In 1938 an instrument, known as the Stereograph (2), was designed and constructed for the purpose of plotting to scale the successive plan projections of the principal points in a strip of air photographs, according to the requirements of the Associate Committee on Survey Research. In addition this instrument was provided with means for the direct measurement of X and Y co-ordinates, parallax, and correspondence errors. It could also be utilized for plotting to scale the true projection of any point or outline depicted in a pair of untilted stereo air photographs.

A magnifying stereoscope was incorporated in the Stereograph, and this feature was found to make it preferable over other available instruments for the actual determination of the plan of the air base on each of successive pairs of vertical air photographs, required for the usual graphical method of radial triangulation. The need for this particular operation became so great in the Air Surveys Office, Department of Mines and Resources, that it prevented the Stereograph from being applied to the metrical and other operations for which it was intended. Accordingly it was decided to make three new instruments for the sole purpose of ruling air bases on the photographs, and which would incorporate those elements of the Stereograph found so useful for this purpose.

Principle

The new instruments were designed by the author and built by the Instrument and Model Shop from working drawings prepared in the Metrology Section. Each consists of a trough-shaped cast-iron base on which are mounted rails supporting and guiding two carriages fitted with pivoted platens to which the photographs can be clipped. Journal type ball bearings form the supporting and guiding members between carriage and rail, in the manner described in Ref. (1). Above the carriages the viewing portion of the fixed stereoscope is supported by a bracket carried from a projection at the back of the base casting.

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Two handwheels are provided. That at the left moves both carriages together along the base direction, and that at the right changes the separation of the two carriages. When the photographs have been correctly oriented, as described below, a straight-edge carried on hinged arms is pulled down so as to be on the platens while the air base projection is ruled in.

FIG. 1.

For the purpose of making this orientation the diaphragms at the focus of the eyepieces are ruled with lines, as shown at (*a*), Fig. 1. If these marks are adjusted by the observer to give good "fusion", when viewed against a white background, he apparently sees a single cross (*b*). By means of the mirror adjustment (2, p. 68) the image of each of the points marking the centres of rotation of the platens can be made to traverse the short line of each mark (*a*). Adjustment of the eccentric ball-bearing arbors at the rear of the carriages permits both centres of rotation to move along the same base direction, if this condition is not already fulfilled.

If, now, a pair of stereo photographs be viewed when correctly set, the cross (*b*) appears to touch the ground in the stereo "model". Change in the separation along the base direction (operation of the right handwheel) will cause the cross apparently to penetrate into or rise from the ground—or, in the case of a large separation, to break into its components. Movement of one photograph relatively to the other in a perpendicular direction will cause the two short lines to become non-linear, i.e., (*c*). If the "weight" of the diaphragm rulings be properly chosen for the average photograph, this phenomenon furnishes an extremely sensitive method for setting a stereo pair into correct fusion. For orienting air photographs on the correctly adjusted instrument by this method, the following program is used.

One photograph carriage is placed and held so that the image of the centre of rotation falls on the intersection of the mark in the appropriate side of the stereoscope. The correct photograph (say *A*) is then clipped on the platen so that its principal point is placed exactly over the centre of rotation, i.e., the image of the cross marked on the photograph is made also to coincide with the intersection of the mark at the focus of the eyepiece. The carriages are now traversed, and the operation repeated for the second photograph *B* of the stereo pair.

Keeping *B* centered, the spacing of the carriages is changed by operating the parallax handwheel until fusion is approached. Lack of correspondence is overcome by slowly rotating *A* with the aid of the tangent screw on the carriage, until the image of the detail at *B*'s principal point seen by viewing *A* is brought into the base direction of the instrument. This condition is reached

when the cross appears as (*b*). In a similar manner, with the principal point of *A* under stereoscopic observation, *B* is rotated into the correct orientation. The direction of the air base can then be ruled with the aid of a needle guided by the straight-edge.

Photograph *B* is then turned 180° in azimuth by rotating its platen, and the third photograph of the strip substituted for *A*, which permits the succeeding air base to be marked on the photographs concerned.

Description

Fig. 2 is a photograph of a completed air-base stereoscope and Fig. 3 shows the same instrument with the platens and lamp removed so that more detail can be seen.

Base.—The main casting is rigid, and is supported through three lugs, one each at the extreme ends near the front and the third at the rear centre. Turned feet are threaded into these lugs. A bracket at the rear, cast integral with the main frame, carries a ribbed casting to support the stereoscope above the photographs. The guide and supporting rails for the carriages are ground on the working faces. To facilitate grinding, these rails were each made in two pieces. The rear rail is dowelled in position while a small bracket is screwed to the front centre of the main frame to support the splice in the front rail. Ball bearings are fitted at all the journal and thrust bearings for the translation and parallax screw and shafts. These bearings are housed in brackets screwed and dowelled to faced pads on the main casting.

Photograph holders.—The photograph holders are essentially the same as those used in the Stereograph (2) except that no provision is made for correspondence settings (motion of the whole platen perpendicular to the base direction).

Translation movement.—For translating both carriages together along the base direction, the left handwheel is coupled by mitre gears to an acme thread screw, inside the main casting.

Parallax movement.—To yield stereoscopic fusion it is necessary to change the spacing of the two carriages as desired. For this purpose the right handwheel drives, through bevel gears, a square shaft behind and parallel to the translation screw. Fig. 4 is a diagrammatic sketch of the mechanism and couplings utilized in providing the necessary movements in such a manner that they can be easily operated and yet be free from backlash.

A, Fig. 4, is the translation screw, *B* the square shaft, and *C* the housing for the nut engaging with *A*. Actually this nut was made in the form of a half-nut, engaged or disengaged by means of the handle seen between the two carriages in Figs. 2 and 3. Practical experience will show whether this feature is worth while. A long sleeve, *D*, Fig. 4, with square-holed bearing portions at each end, is free to slide along *B*. For most of its length *D* is cut with a vee thread of 20 t.p.i., and engages with a long nut, *E*, which is split on one

FIG. 2. *A complete air-base stereoscope.*

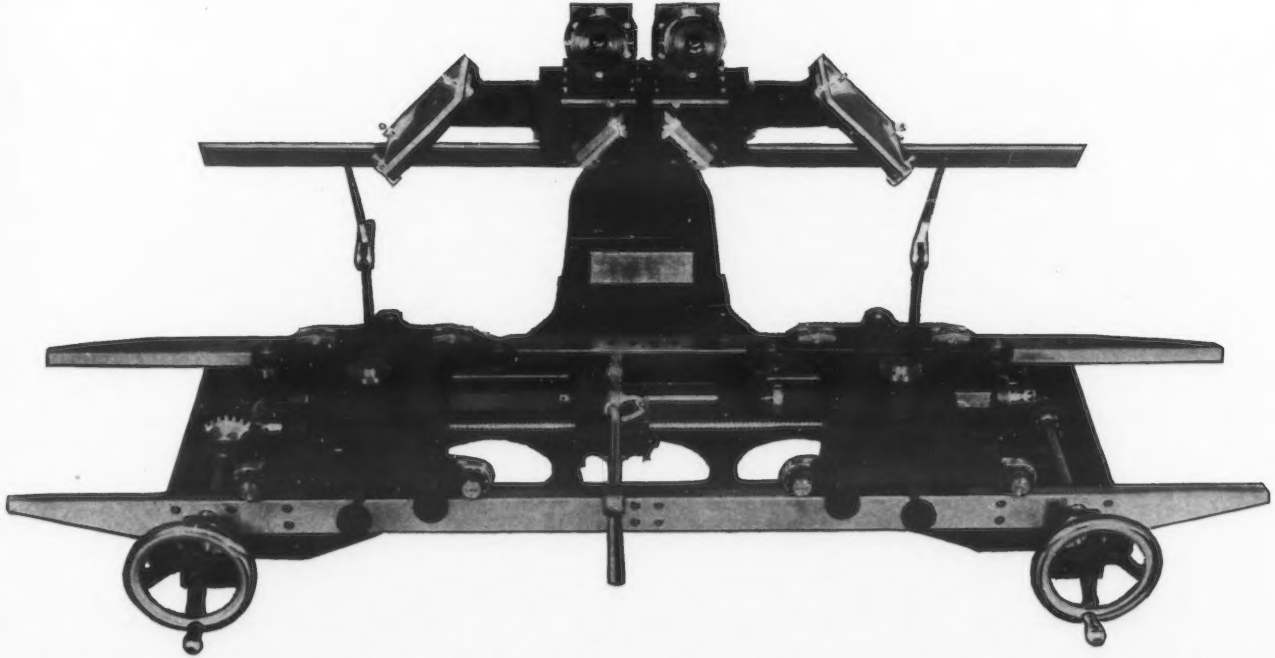

FIG. 3. *The instrument partially stripped to show more of the working parts. The handwheel to the left operates the translation screw, moving both carriages together along the rails. Operation of the right handwheel changes the separation of the two carriages. The handle seen at the lower centre engages or disengages the translation nut, when quick hand movement along the rails is desired. The black knobs in front of each carriage are on the clamping and slow motion tangent screws of the platen pivots.*

side and fitted with screws for taking up wear. It can be seen from the diagram that rotation of *B* will cause the nut *E* to move along *D*, while the whole assembly can slide freely along *B*, under the control of *A*.

To avoid unnecessary frictional or jamming resistance both nuts are constrained only in the sense preventing rotation about the axes of their respective screws. Thus, *C* is fitted with two lugs, *F*, provided with holes engaging pins

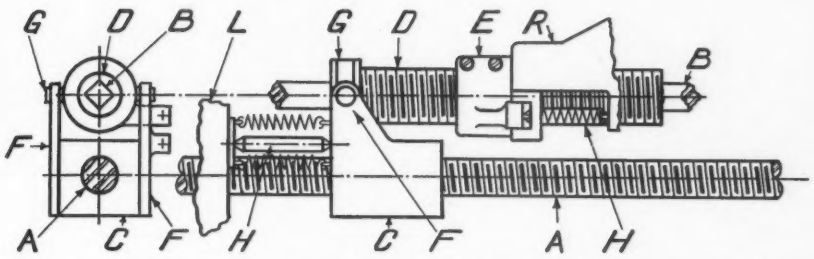

FIG. 4. *Diagram to illustrate the translation and coupling mechanism for the photograph carriages.*

turned on a collar, *G*, which runs in a groove on *D*, and makes contact only at the top and bottom of the cylindric portion of the groove. The rotation of nut *E* is prevented by a lug integral with it, and engaging with a groove in a plate attached to the right carriage. Pointed struts, *H*, with spring closure, are used to impart pure translation movement to the respective carriages, *R* and *L*.

The whole assembly operates very successfully. Lost motion is inappreciable, and yet the lightest finger touch on either handwheel will move the photographs.

Stereoscope.—The optical portion of the instrument is almost an exact copy of the similar part of the Stereograph (2). The elements, including front surfaced mirrors, were made entirely in the Optics Section of the Division. To facilitate viewing, a pair of small fluorescent lamps is mounted in a cover seen just beneath the mirrors in Fig. 2.

Straight-edge.—The straight-edge is attached to arms as seen in Figs. 2 and 3. Normally it is held conveniently out of the way against the stereoscope-supporting bracket, by means of a spring and ball fitted to the hinge. It can be brought down on to the photographs as desired, and nuts are provided at the base of the fixed vertical hinge arms, for use in adjusting the edge to the line of centres of the platens.

Acknowledgment

Messrs. G. C. MacKiddie and W. C. May, of the Instrument and Model Shop, built the three air-base stereoscopes here described. They introduced a number of improvements to details of the design which contributed materially

to the successful functioning of the instruments. Messrs. R. B. McKay and J. Carroll, of the Department of Mines and Resources, gave valuable advice from the operational point of view.

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A DIVIDING HEAD FOR LABORATORY USE[1]

By R. H. Field[2]

Abstract

The description is given of an easily constructed dividing head that embodies the circles and other parts of discarded theodolites. Originally designed for facilitating the inspection of munitions gauges, the instrument was found to have other valuable applications in metrology. In the appendix there is an account of the method used to calibrate the graduated circle of one of these "angle-heads", in which angles are read to single seconds of arc.

Purpose

The dividing heads here described, and called "angle-heads", were designed early in Great War II for simplifying problems presented by various types of munitions gauges where rectangular and polar co-ordinates (often in combination) have to be measured during inspection. Measurement of these gauges usually entails a more or less extended time on the part of relatively highly skilled personnel, particularly if devices of the type under consideration are not available. The angle-head was also found useful for other purposes, notably in the calibration of clinometers, and several were made during the recent war for use in the National Research Laboratories. For these instruments the graduated circles and other parts were obtained from discarded theodolites; this greatly reduced the cost and time for the construction.

First Model

The first angle-head made is illustrated in Fig. 1. The base is of cast-iron, massive, and stiffened by a web joining the two bearing housings. On the bottom are three scraped supporting pads, which, when the angle-head is assembled, have their common plane accurately parallel to the axis of the spindle. Bronze is used for the split bushings, which are hand-scraped. One bearing is of the journal type, with collars turned on the steel spindle. The tail end of the spindle is bored to fit the cone of the lower portion of an old transit, having a tolerably good horizontal circle. For the adaptation the only special parts required were a small bracket and opposing screws, to locate and adjust the vernier fitting of the transit.

The faceplate is 8 in. diam. and made of cast-iron. It was finally surfaced in the lathe after fitting on the spindle, and is secured by screws tapped into the outer collar. A series of tapped holes is distributed over the faceplate to permit the clamping of fastenings, gauges, etc., as required, and there is also a groove milled across the centre and finished so as to have its sides symmetrical with respect to the spindle axis. Two small brackets fitted with

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centres can be located in this groove, and clamped to the faceplate, for the purpose of holding, say, small taper gauges with centre-holes. The head end of the spindle is bored to receive a standard lathe centre. As a rod cannot be used to remove this centre, it is machined with a collar to facilitate extraction. The tailstock, seen to the right of the faceplate in Fig. 1, is used in conjunction with the angle-head, for indexing or measuring work carried by two centres.

A groove 3/8 in. wide is turned in the spindle of the angle-head between the bearings, to locate the clamp. This is of bronze and split for assembly purposes. The lower half is relieved so as to contact the surface of the groove over two small areas, spaced 120° apart. The clamping shoe is made an accurate fit in a slot formed in the upper half, and is closed by means of a knurled-head screw. With these parts properly fitted, a positive clamping action, with no rotation imparted to the spindle, is attained by light finger operation of the screw.

Slow rotation of the spindle is given by a 0.375 in. × 24 t.p.i. screw, which is bored up the centre and fitted with a round-ended strut. The outer end of the strut fits into a cupped recess at one end of a horizontal lever, pivoted to the base at the other end. Near the centre of the lever a second strut imparts movement to the tail of the clamp. Closure is maintained by a compression spring in a tube on the far side of the web in the main casting. A pin couples this spring to a recess in the clamp tail. By these means a steady slow-motion is obtained free from jerks or irregularities.

Application

Many uses for this appliance come at once to the minds of toolmakers and inspectors. Recently the theory and practice of many of these applications have been published by Barnard (1), and so need not be discussed here.

An important constant is the height of the spindle axis above the plane of the three pads, which has to be determined with the aid of a mandrel of measured diameter, by obvious methods.

Precision Model

The need for the calibration of precision clinometers and other work where an accuracy of one or two seconds of arc was necessary led to the building of a larger instrument, which is illustrated in Fig. 2. It was designed to take the 300 mm. diam. graduated circle and reading microscopes of a primary triangulation theodolite. In this case a 10 in. diam. faceplate was fitted to each end of the spindle, that at the circle end being threaded on, after the fashion of a lathe faceplate. A long tangent screw, threaded 50 t.p.i., is used, acting directly, in this case, on the tail of the clamp through a spherical-ended steel strut, bearing against a hard recessed shoe, inserted in a hole in the screw. A tension spring maintains closure, and is hooked to the middle of a horizontal lever on the far side of the central web. Pressure from the

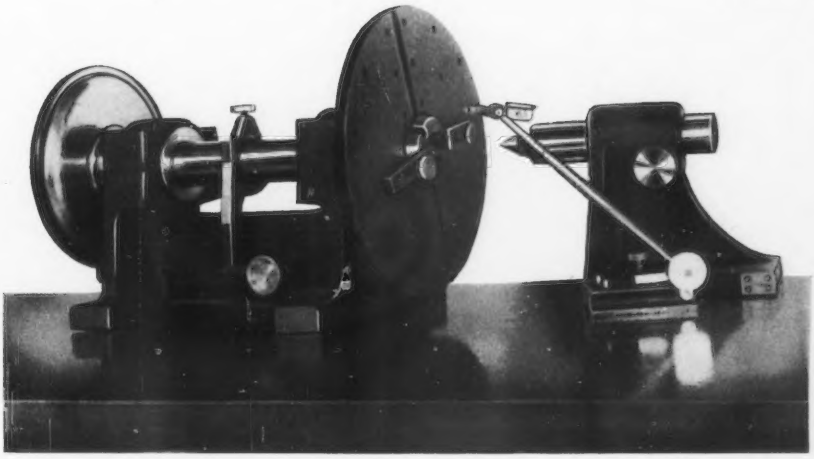

FIG. 1. *First model, angle-head, with circle reading to one minute.*

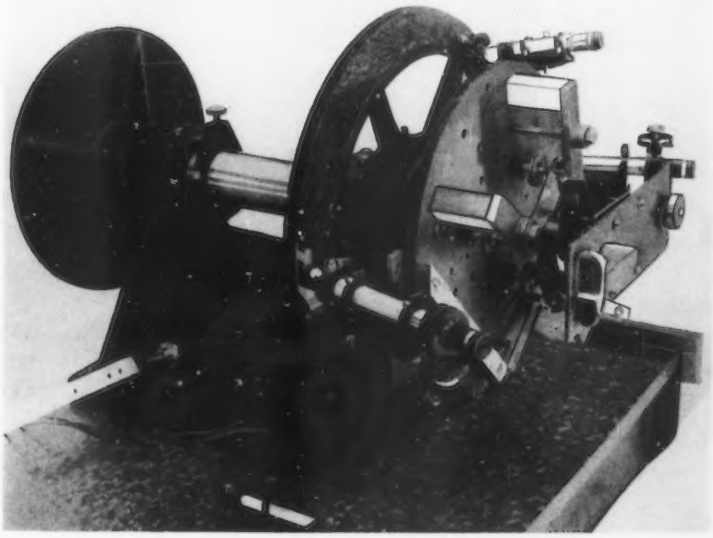

FIG. 2. *Second model, angle-head, with two faceplates and circle reading to one second. In this view the right faceplate carries the mounting and prisms used for the calibration of the circle by the method described in the Appendix.*

end of the lever to the clamp tail is transmitted through a second strut, located in conical recesses in the lever-end and clamp tail.

The circle is graduated at 5′ intervals, one division of the microscope drums being equivalent to 1″. This circle was calibrated after the instrument was completed, by the method described in the appendix.

APPENDIX

Calibration of the Divided Circle of the Large Angle-head

Principle

Expression for a reading.—It is shown in textbooks on astronomy, e.g., (2, Chap. II), that the general expression for the readings of the respective two *exactly* opposite verniers (or micrometer microscopes) on the alidade of a divided circle are:

$$A = Z - e \sin (Z + E) + \epsilon_z \qquad (1)$$

and

$$B = 180° + Z - e \sin (180° + Z + E) + \epsilon_{180° + z}, \qquad (2)$$

where Z = The reading if the alidade were exactly centered with respect to the circle and if the graduations were correctly placed;

e = The eccentricity, i.e., the angle subtended by the line joining the centre of the circle and the axis of rotation of the alidade, at the circumference of the circle;

E = The azimuth (on the circle) of the line just mentioned;

ϵ_z = The error in the position of the graduation at the nominal angle, Z, on the circle.

Eccentricity.—Hence the mean reading $(A + B)/2$ is independent of the errors due to eccentricity, and involves the mean of the two opposite graduation errors. It would also appear from the theory that a variable eccentricity, e.g., such as would be introduced by a departure of the alidade pivot from true cylindrical or conical form, or by looseness in the fit of that pivot, would have no effect on the mean of the two readings. That is, provided this fit is not too tight when, as has been shown by Rannie (3), important errors are introduced; the degree of perfection in the fit of the alidade pivot may not be of first order importance provided both verniers are read at each observation. It also follows from Equations 1 and 2 that in calibrating a circle having opposite verniers, the observations can be limited to an arc of 180°. In certain cases, however, as with some of the observations described below, the calibration test is carried right around the circle for check purposes. The values of E and e can be obtained from the readings made in the course of the tests described below or, as was actually done in this case, in a special test, from reading the two micrometers at a number of points distributed around the circle. Actually E and e have only to be known if subsequently angles are to be measured by means of a single vernier. They also are required

if the value of ϵ is to be determined throughout the 360°, e.g., to assess the degree of perfection attained in the circle-graduating operation.

Graduation errors.—A circle graduated throughout its circumference contains by definition exactly 360°, beginning and ending at any single graduation mark. Therefore, one of the main difficulties in many types of instrument calibration—the comparison with an accepted reference standard— is overcome. It is merely necessary to find some constant external reference angle that is nearly an exact submultiple, say $1/n$, of, first 360° and subsequently, of the subdivisions already calibrated, and to compare this reference angle successively with each of the n equal parts of the circle or interval under study. By suitably drawing up the test program, it is generally necessary that the reference angle remain constant for only a short time. As a further refinement, by making the n observations first in the one direction and immediately afterwards in the reverse order, it can usually be assumed, without serious error, that any small change in the reference angle has been taking place at a uniform rate during the observations, and so is eliminated in the means.

Computation

Using the notation of Equations 1 and 2, we find the expression for the micrometer readings at the two points subtending an angle $Z_1 - Z = \phi$ on the circle to be:

$$A_{z_1} + B_{z_1} - A_z - B_z - \epsilon_{z_1} + \epsilon_z - \epsilon_{180^\circ + z_1} + \epsilon_{180^\circ + z} = 2\phi \,. \qquad (3)$$

Considering the diametral mean reading, R_z, and the diametral mean error, ϵ'_z, for a given pair of observations, Equation 3 becomes:

$$R_{z_1} - R_z - \epsilon'_{z_1} + \epsilon'_z = \phi \,. \qquad (4)$$

In the actual tests a series of n such pairs of observations is made, and the sum of the n equations, 4, is:

$$R_{n\phi} - R_0 - \epsilon'_{n\phi} + \epsilon'_0 = n\phi \,. \qquad (5)$$

In the first test $n\phi$ is chosen so as to be nearly 360°, and hence $\epsilon'_{n\phi} = \epsilon'_0$ and

$$\phi = (R_{n\phi} - R_0)/n \qquad (6)$$

Inserting this value of ϕ in the first of the set of Equations 4, the value of ϵ'_ϕ is determined, and this value permits the value of $\epsilon'_{2\phi}$ in the second equation to be found and so on. Actually it is not necessary that the initial reading in each measurement of ϕ coincide exactly with the final reading of the preceding measurement, and ϕ can be obtained from the mean of the n measurements. A very simple tabulation suffices for the computation as shown in the example (Table I). The process can be extended down to the smallest graduation interval on the circle.

The values of E and e, as well as the small angle, α, by which the spacing of the fiducial points of the micrometer microscopes differs from 180° (Equations 1 and 2), can be found (2) from reading the two micrometers at a suffi-

TABLE I

CIRCLE CALIBRATION

TYPICAL SET OF OBSERVATIONS, AND REDUCTION

Observations																							
Microscope *A*				Microscope *B*				Mn	Mn *F* and *B*	Δ	Σ (Δ)	* Interval correction	Diametral correction	
Reading			Diff.	Reading			Diff.							
0°	01′	32″	″	180°	02′	20″	″	″	″	″	″	″	″	
3	01	49	17	183	02	34	14	15.5	16.2	−1.6	−1.6	+0.6	−1.0	(3°)
3	01	45		183	02	15								
6	01	30	15	186	02	28	13	14.0	14.5	+0.1	−1.5	+1.2	−0.3	(6°)
6	01	30		186	02	14								
9	01	45	15	189	02	27	13	14.0	13.2	+1.4	−0.1	+1.8	+1.7	(9°)
9	00	51		189	01	33								
12	01	05	14	192	01	47	14	14.0	14.0	+0.6	+0.5	+2.4	+2.9	(12°)
12	00	44		192	01	26								
15	00	59	15	195	01	40	14	14.5	15.2	−0.6	−0.1	+3.0	+3.0	(15°)
							Mean, ϕ = 3°00′ 14″.6							
15	01	08		195	01	48								
12	00	51	17	192	01	33	15	16.0						
12	00	39		192	01	20								
9	00	24	15	189	01	07	13	14.0						
9	01	42		189	02	26								
6	01	29	13	186	02	14	12	12.5						
6	01	14		186	01	59								
3	00	58	16	183	01	45	14	15.0						
3	01	55		183	02	42								
0	01	36	19	180	02	27	15	17.0						

*From previous tests:—

Correction at 0° = 0″
Correction at 15° = +3″.0
3″.0 ÷ 5 = 0″.6

ciently large number of points around the circle to compensate for the effect of the graduation errors. Values can then be calculated for the individual residual errors ϵ_z in Equations 1 and 2, after substituting the now known quantities.

APPARATUS

The reference angles, ϕ, were obtained by mounting two prisms with aluminized working faces on the angle-head, setting the faces at the desired angle to one another and using an autocollimator to bring the faces successively into the same position, i.e., normal to the axis of the fixed collimator.

The photograph of the precision angle-head, Fig. 2, actually shows the prisms and auxiliary apparatus mounted in position for part of the calibration test. This test was carried out with the aid of the regular collimator system of the Metrology Laboratory. In this apparatus the collimators are sup-

ported on massive concrete piers, resting on the underlying rock, in an air-conditioned room below ground level. No appreciable change in the direction of the collimators can be detected over extended periods, so they serve excellently as fixed reference directions in tests of this kind. A reflecting eye-piece was fitted to the horizontal collimator utilized in this particular case. The angle-head was set up on a levelling base placed on the regular testing stand, at the centre of the collimator system, in order that its spindle could be made horizontal and placed approximately normal to, and at the same height as, the axis of the collimator.

It was necessary so to mount the prisms that they could be readily adjusted with their faces parallel to the spindle axis of the angle-head and could be turned around as a unit after the measurement of each angle ϕ. For this purpose the tribrach and horizontal limb of a discarded small mountain transit was mounted on the faceplate, as seen in Fig. 2. At first some irregularities were found in the readings, but these were traced to looseness in the conical centres of the old tribrach. They were overcome by fitting a nut that permitted the cones to be drawn tight after the setting of the prism assembly at the beginning of each of the n measurements.

In the actual test one observer set the initial position of the prism assembly nearly correct, under the command of a second observer at the collimator eye-piece. He then clamped the cones of the small tribrach, and observer No. 2, with the aid of a wooden rod temporarily clamped to the head of the angle-head tangent screw, brought into coincidence the collimator cross wires and the image of the wires reflected from the first prism face. Observer No. 1 then read both angle-head micrometers. He next unclamped the angle-head, rotated the faceplate through, approximately, the angle ϕ, clamped it, and observer No. 2 brought on to the cross wires the image reflected from the second prism face. Finally, observer No. 1 again read the two micrometer microscopes. This program permitted the test to be carried out quite rapidly.

A typical example of the readings and their reduction for the interval 0° to 15° is given in Table I.

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NOTES ON THE TESTING OF SEXTANTS[1]

By G. O. West[2]

Abstract

In World War II a shortage of mariners' sextants resulted in the collection by the Royal Canadian Navy of used sextants from various sources. These were, as far as possible, reconditioned and verified by the National Research Laboratories, Ottawa. For this work, and for calibrating new sextants, some modifications were made to the collimator system regularly employed for the verification of angle-measuring instruments. A brief description is given of the apparatus and of the procedure developed for testing sextants, together with a few remarks on sextant errors.

Introduction

During the recent war, there was an urgent demand for mariners' sextants, and the Royal Canadian Navy collected a number of second-hand instruments, which were reconditioned and calibrated at the National Research Laboratories. Also, during the war a Montreal firm designed and constructed a dividing engine for cutting the arcs of sextants, and consequently was able to undertake the manufacture of new instruments. Representatives of the firm came to the Laboratories from time to time for advice, and some of their sextants (the first, so far as is known, to be built in Canada) were subsequently submitted to the Laboratories for certification.

Only a few mariners' sextants had been calibrated prior to the war. These were verified for the accuracy of their angular indications by measuring with the sextants the angles subtended by church spires, chimneys, and other suitable distant objects, visible from the roof of the Laboratories, the angular distances between these various targets having first been determined by means of a theodolite. Under the new conditions imposed by the war, it became imperative to devise an indoor test for greater speed and accuracy, and for independence from weather conditions.

This was done by additions to the collimator system already in use for testing transits, levels, and other optical measuring instruments. This apparatus, which is now installed in the National Research Laboratories, was devised originally about 1910 by the well known former Surveyor-General of Canada, Dr. E. G. Deville (1).

The theory of the sextant is set out in textbooks on astronomy and surveying (2), and it is there shown that instrumental errors may be due to defects in:—

1. The perpendicularity of the index mirror to the plane of the arc,
2. The perpendicularity of the index axis to the plane of the arc,
3. The parallelism of the line of collimation of the telescope to the plane of the arc,

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[2] *Technical Officer.*

4. The perpendicularity of the horizon glass to the plane of the arc,
5. The graduations on the arc (or, in the case of modern sextants, the spacing of the sector teeth),
6. The optical characteristics of the mirrors and shades.

A slight modification of the usual collimator set-up as employed for the calibration of most other instruments for measuring angles is required in the case of sextants, owing to the fact that the two direction lines (which determine the angle under observation) do not intersect at the geometric centre of the measuring arc.

At the National Physical Laboratory in England, sextant tests are carried out with the aid of a set of collimators mounted in pairs (the two units of a pair being parallel) on a hollow cast-iron arc through which water is circulated to maintain a constant temperature. As a simpler alternative, it was decided in the present case to make single collimators radiate from the centre of the testing platform, but to support the sextant horizontally on the platform in such a way that it could readily be moved, so that the axes of the two collimators under observation at a given time could be made to intersect the centres of the respective sextant mirrors. Thus the use of duplicate collimators was avoided—the sextant being recentred for each angle. This adjustment is readily made by eye to a precision that does not affect the accuracy of the angles for properly focused collimators.

Apparatus

The collimators, Fig. 1, which are located in an air-conditioned room in the sub-basement of the Laboratories, are set on concrete piers isolated from the floor and resting on the bed rock. The cast-iron supports in which the telescopes are mounted are each carried by three foot-screws. Discarded surveying instruments were utilized in making the additional collimators needed for verifying sextants.

The special table supporting the sextants to be tested is rigidly attached to the top of the vertical axis of an old triangulation theodolite base, visible in Fig. 1. This assembly rests on the regular testing platform, which is at the intersection of the collimator axes, and is adjustable for height. The sextant table can be adjusted for horizontality by means of the foot-screws of the theodolite base and can also be turned in azimuth and set in any required orientation by the tangent screw assembly.

Fig. 2 is a plan diagram of the collimator arrangement that is seen in Fig. 1.

The angular distances between the various collimators that are used to determine the errors of graduation of a sextant are approximately as follows:—

E to *D*	15°	*H* to *F*	75°
F to *E*	30°	*F* to *A*	90°
F to *D*	45°	*H* to *E*	105°
A to *E*	60°	*H* to *D*	120°

PLATE I

FIG. 1. *Collimator system for testing sextants. The larger collimators seen were already in use for other purposes. Additional smaller collimators were made from discarded surveying instruments. A modern sextant is shown under test. On the pier is an old wooden octant submitted to the Navy during the war.*

Collimator *G* is used only in testing the shades, and collimator *C*, which has a large objective, is employed for setting the zero position of the vernier or drum.

For targets, thin metal diaphragms with slots were first tried in the new collimators, but better results were obtained with graticules carrying cross

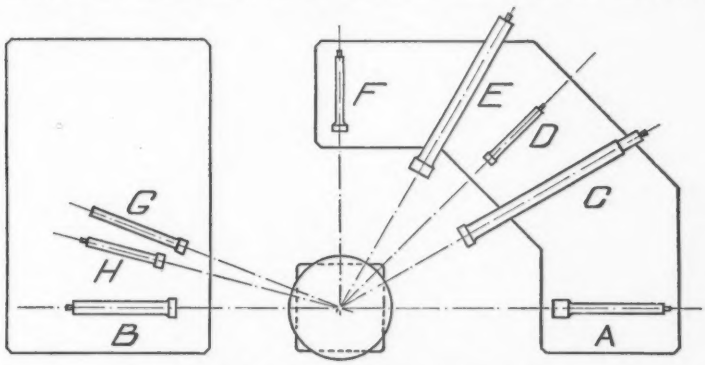

FIG. 2. *Diagrammatic plan of the collimator system.*

lines of fine tungsten (lamp filament) wire. When measuring a given angle the arrangement permits the single vertical wire in the image from one collimator to be set midway between the pair of wires in the image from the second collimator.

Collimator *E* is fitted with a special glass diaphragm on which, in addition to a pair of vertical lines, seven nearly equidistant vertical lines are ruled. This glass diaphragm was made specially for the purpose by the Optics Section. These seven lines are spaced at 10′ intervals and are used for measuring the progressive errors of micrometer screws.

All the cross wires are illuminated by 10-v. lamps with ground glass diffusers. The intensity of each light can be changed by means of a variable rheostat in a control panel adjacent to the observer and visible in Fig. 1.

Test Program

The following test program was adopted, based in part on classical methods, but with some modifications that are thought to be original.

(*a*) *Preliminary Examination*

The sextant is first examined for obvious defects. Some of the major faults that are encountered include, for example: lack of coincidence in the graduations of the vernier and arc; backlash in the tangent screw assembly; parallax in reading the scale in the case of graduated instruments; and incorrect mating of the cone worm with the sector in micrometer sextants.

(*b*) *Perpendicularity of the Index Mirror and Pivot*

To check these errors, the sextant, with the telescope assembly removed, is set up on the levelling table with the index mirror between collimators

A and *B*, whose optical axes are coincident and truly horizontal. An auto-collimating eyepiece, replacing the lamp, is fitted to each of the collimators.

First the sextant is adjusted so that the horizontal cross wires of *B* and their reflected image from the index mirror, as seen by an observer looking through the eyepiece of *B*, are coincident. In this position the index mirror is truly vertical. The index arm is then rotated 180° in azimuth. If the horizontal cross wires and their reflected image, as seen by an observer looking through the eyepiece of *A*, do not coincide, half the discrepancy is taken up by the foot-screws of the theodolite base and half by the adjusting screws on the frame of the index mirror.

When this adjustment is completed the plane of the index mirror and the pivot (unless the pivot is distorted) will be truly vertical when the mirror is at right angles to the line of collimation of the telescopes.

The perpendicularity of the index axis to the plane of the arc can now be tested. This can quickly be done with the aid of a small spirit level laid on the graduated surface of the arc, at the same time keeping the index mirror truly vertical for any desired position of the sextant, by adjusting the foot-screws of the theodolite base and observing through the reflecting eyepiece of one of the collimators *A* or *B*.

(*c*) *Parallelism of the Telescope*

With the telescope assembly restored to the instrument, the telescope is directed on collimator *B*, the graduated surface of the arc of the sextant being brought truly horizontal with the aid of the small spirit level. If the line of collimation of the telescope is parallel to the plane of the arc, the image of the cross wires of *B*, when viewed through the telescope, will be in the centre of the field of view. Any necessary adjustment is made by means of the two adjusting screws on the ring carrying the telescope.

(*d*) *Perpendicularity of the Horizon Glass*

The sextant is directed on collimator *C*. This collimator has an aperture of 80 mm. and is therefore large enough to include parallel rays to both the index mirror and horizon glass of an ordinary sextant. The vernier being set to zero, the horizon glass is then adjusted to bring the images of the horizontal and vertical cross wires into coincidence.

(*e*) *Graduations on the Arc*

When checking sextant indications for the angular distances between various collimators, a telescope of ×10 magnification, with adapters to fit different types of sextants, is used so as to avoid eyestrain. The angles between the collimators remain constant for several hours and can be measured very quickly, when required, by means of a Wild theodolite reading to single seconds, and which can be set up on the regular testing stand.

(*f*) *Mirrors and Shades*

A complete description of the effect of errors introduced by prismatic mirrors is given in Reference (2, p. 83). In the laboratories the back-surfaced

mirrors are tested individually to determine whether their faces are truly parallel. The lamp for collimator *B* is replaced by a Ramsden eyepiece. The sextant is adjusted on the levelling table so that each mirror in turn is placed at the intersection of the optical axis of *B* and that of one of the collimators with a relatively large angular distance from *B*, and so that the image of the cross wires can be seen by an observer looking through the eyepiece of *B*. If a mirror is prismatic a ghost image of the cross wires will also be seen. The method adopted for determining the prismatic errors of the shades is practically the same as that employed by the National Physical Laboratory. The angular distance between collimator *G*, which carries a thin metal diaphragm with a pair of vertical slits to admit the light, and collimator *B*, which has a small illuminated hole in the comb of the diaphragm, is measured by the sextant without the use of shades. Each shade is then separately introduced. Any prismatic error is measured directly by the vernier (or drum) of the sextant. Brighter lights are of necessity used on these two collimators for this purpose, the intensity of the light depending on the density of the shade being tested. For very dense shades a 900 w. condensed filament light may be necessary.

If the faces of the mirrors are not truly plane the definition of the image of the cross wires, when viewed through the high power telescope, will be distorted. In cases where such distortion is suspected the actual flatness of the mirrors is investigated by interferometric means.

(*g*) *Progressive Errors in Micrometer Screws*

The angular distances between the seven extra vertical lines in collimator *E* and the pair of vertical lines in collimator *F* are measured by the sextant. The progressive error of the micrometer screw is determined by comparing the sextant indications of the successive increments, which give a complete turn of the screw at 10′ intervals, with the known values which were originally measured with the Wild theodolite.

Some Remarks on the Second-hand Instruments Submitted by the Navy

Some of the second-hand instruments received from the Navy were found to be considerably damaged, probably as the result of being dropped, and these presented some problems for the instrument-maker. A sextant with a bent arc or bent pivot socket is difficult to restore to its original condition. The makers usually graduate the arc after the pivot axis has been fitted.

The mirrors from these used instruments were, when necessary, resilvered. A few of them, which gave poor images of the cross wires, were found on interferometric examination to be plane. The trouble was traced to their not being properly supported in the mirror frames. If the spring clips holding the mirror in place are not directly over the studs supporting the mirror, even light pressure of the adjusting screw may cause distortion. One mirror was found on examination to be of ordinary window glass.

These second-hand instruments were an interesting assortment. One modern German sextant fitted with a micrometer drum was found to be in excellent condition and to have negligible corrections for both the angular indications and the shades. This instrument proved to be the best sextant ever tested here. The graduations on the arc of another sextant had obviously been stoned off and then restored with the aid of a pocket knife or similar instrument. On still another instrument, initials had been carved on the arc in such a way as to obliterate some of the graduations. Also included was an octant such as was used by mariners in bygone days. This instrument, of English manufacture, with an ebony frame and an ivory scale graduated by hand, is visible on the pier in Fig. 1.

Acknowledgment

The extra collimators and the levelling table for supporting the sextants were constructed by Mr. A. A. Barks of the Division of Physics and Electrical Engineering. His assistance and advice are gratefully acknowledged.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XI. EVALUATION OF *LEVO*-2,3-BUTANEDIOL AS A NON-VOLATILE ANTIFREEZE COMPOUND[1]

By K. A. Clendenning[2]

Abstract

levo-2,3-Butanediol is more effective than glycerol and less effective than ethylene glycol as a freezing point depressant for water. The considerable discrepancy that is reported between observed freezing points and values calculated from Raoult's law for solutions of these chemicals is attributed to hydration. The antifreeze property of *levo*-2,3-butanediol is not impaired by prolonged refluxing or by use in automobile cooling systems. The viscosity of 50 to 60% solutions is considerably greater than that of 50 to 60% ethylene glycol and is slightly greater than that of 50 to 60% glycerol at 20° C., the differences in viscosity between these solutions being magnified by low temperatures. Kinematic viscosity data are presented for *levo*-2,3-butanediol solutions at concentration intervals of 10% over the greater part of the liquid range.

The comparatively low surface tension of *levo*-2,3-butanediol solutions indicates a possible need for precautionary measures against creeping and foaming. Metallic corrosion is not greater than with water, barring excessive contamination with acetates. *levo*-2,3-Butanediol and ethylene glycol are judged equally satisfactory with respect to heat capacity, flash point, expansion on solidification and heating, and effects on metal finishes and rubber. Density of *levo*-2,3-butanediol solutions cannot be used as a measure of freezing point protection. The mixtures of 2,3-butanediol isomers obtained with *Aerobacter aerogenes*, *Aeromonas hydrophila*, and *Bacillus subtilis* are lacking in antifreeze properties because of their high content of the *meso*-isomer.

Introduction

The usefulness of 2,3-butanediol as a potential source of synthetic rubber prompted a vast amount of research on its production by bacterial fermentation, as well as on its purification, esterification, and pyrolysis to butadiene. Experimentation was extended to pilot plant studies at several laboratories, and commercial developments in all likelihood would have followed had other sources of synthetic rubber proved inadequate.

Several patents have been granted in which some mention is made of the usefulness of butanediol as an antifreeze (11, 14, 28). Information was not provided at the time of their issue, however, on the relative usefulness of the eight different butanediol isomers that are of interest in this application. Michael and Hopkins (20) have indicated that 1,3-butanediol is unsuitable because of the extremely high viscosity of its solutions at low temperatures. The 2,3-butanediol that is produced by *Aerobacter aerogenes* (4), *Aeromonas hydrophila* (30), and *Bacillus subtilis* (23) consists of a mixture of isomers in which the *meso*-form predominates. The diol produced by *Aerobacillus polymyxa* consists entirely of the levorotatory isomer (22, 34). Chadderton

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[2] *Biochemist, Industrial Utilization Investigations.*

and Cook* observed that *levo*-2,3-butanediol has valuable antifreeze characteristics, and that these are lacking in the corresponding *meso*-isomer. Reference has also been made to the differences in antifreeze properties of 2,3-butanediol isomers by Ward, Pettijohn, Lockwood, and Coghill (34).

The popularity of an antifreeze is largely decided by the yearly expense that its use entails. Since *levo*-2,3-butanediol combines the advantage of permanence shown by ethylene glycol with a potentially low selling price, its possibilities in the antifreeze field deserve attention. The present paper reports a study of those properties of its aqueous solutions that have greatest bearing upon usefulness and performance in automobile cooling systems.

Materials and Methods

The *levo*-2,3-butanediol samples were prepared from fermented wheat mashes by methods outlined elsewhere (22, 27). The mixed isomers ($[\alpha]_D^{25} = +0.8°$) obtained with *Aerobacter aerogenes* consisted of the *meso*-form and 5 to 10% of the *dextro*-isomer. The 2,3-butanediol samples obtained with *Aeromonas hydrophila* and *Bacillus subtilis* had $[\alpha]_D^{25}$ values of $-1.25°$ and $-4.86°$ respectively. The water content of *levo*-2,3-butanediol samples was determined by reference to tables of refractometric and polarimetric data (5). Degree of contamination with esterified acetic acid was determined by a method based on saponification and back titration (21). Ethylene glycol was purified by fractional distillation *in vacuo*, the fraction selected for use showing a refractive index of 1.4320 at 25° C. Glycerol of c.p. grade was used as received, its water content being determined by measurement of the refractive index. Absolute ethanol and synthetic methanol were redistilled at atmospheric pressure before use. All solutions were made up by accurate weighing.

The freezing points were determined by the conventional procedure of supercooling the solutions, seeding with a few crystals of the appropriate component, and following the resulting temperature change by thermocouple. It was found advantageous to run a series of determinations on different samples of the same solution, seeding each at the apparent freezing point of the previous sample, the values as here recorded referring to the highest temperature at which incipient crystallization could be induced in this manner. An auxiliary unit similar to the freezing point apparatus described by Cummings (7) was used in confirming freezing point values by visual inspection. The accuracy of the determinations is considered to be of the order of 0.2° C. except at the lowest temperatures, where the possible error is judged to be 1° to 2° C. The temperature at which *levo*-2,3-butanediol solutions become solid is several degrees below that at which incipient crystallization occurs on seeding; e.g., the 50% solution, which shows a freezing point of −29.6° C., reaches the consistency of moist taffy at −36° to −37° C. This property and the pronounced supercooling tendency of diol solutions is judged to offer a con-

* *Unpublished report, December, 1942.*

siderable margin of safety against solidification at the recorded freezing temperatures.

The viscosity measurements were made by the conventional kinematic method (1), using Ostwald viscosimeters immersed in constant temperature baths. Absolute viscosity was calculated by the use of specific gravity data reported elsewhere (5). Boiling points were determined in an apparatus equipped with a Cottrel pump and N.B.S. certified thermometer. Flash point was estimated by the A.S.T.M. open cup method (1). Surface tension measurements were made at 25° C. with a Du Nuoy interfacial tensiometer. Corrosiveness was assessed by the changes in weight and appearance of metal test plates after two months' immersion at room temperature. Solvent action on automobile finishes was tested by immersing variously coated steel rods in the antifreeze compounds and solutions, and observing the condition of the protective finishes after 90 min. exposure at room temperature. Effects on rubber hose connections were determined by immersing rubber samples in the antifreeze solutions for three days at 80° C. and noting the changes in physical properties by conventional objective methods.

Results and Discussion

In its major features, the freezing point curve for *levo*-2,3-butanediol in water (Fig. 1) corresponds closely to similarly expressed data for ethylene glycol and glycerol. As Table I shows, *levo*-2,3-butanediol is intermediate

TABLE I

FREEZING POINT DATA FOR METHANOL, ETHANOL, ETHYLENE GLYCOL, GLYCEROL, AND *levo*-2,3-BUTANEDIOL SOLUTIONS

Solute by weight, %	Methanol		Ethanol		Ethylene glycol		Glycerol		*levo*-2,3-Butanediol	
	F.p. observed, °C.	F.p.* calculated, °C.	F.p. observed, °C.	F.p.* calculated, °C.	F.p. observed, °C.	F.p.* calculated, °C.	F.p.** observed, °C.	F.p.* calculated, °C.	F.p. observed, °C.	F.p.* calculated, °C.
10	− 6.3	− 6.46	− 4.5	− 4.49	− 3.6	− 3.33	− 2.0	− 2.25	− 3.1	− 2.30
20	−15.3	−14.5	−10.5	−10.1	− 8.3	− 8.27	− 5.2	− 5.05	− 7.1	− 5.17
30	−26.3	−24.9	−20.0	−17.3	−14.7	−12.9	− 9.9	− 8.67	−12.4	− 8.85
40	−39.7	−38.8	−29.4	−27.0	−23.5	−20.0	−15.9	−12.0	−19.4	−14.3
50	−55.2	−58.1	−37.0	−40.4	−35.0	−30.0	−24.6	−20.2	−29.6	−20.7
60			−43.8	−60.7	−50	−45.0	−37.9	−30.3	−40.4	−31.0

* $\Delta = \frac{K\ 100\ n}{g}$, *where* Δ = *F.p. lowering,* K = *f.p. lowering for 1 mole solute in 100 gm. solvent (18.6° C.),* n = *number of moles solute,* g = *grams solvent.*

** *Data of J. A. Spangler and E. C. H. Davis. Ind. Eng. Chem., Anal. Ed. 15 : 96-99. 1943.*

between these two chemicals as a freezing point depressant for water, while ethanol and methanol depress the freezing point to a greater extent at equivalent percentages by weight.

Antifreeze solutions represent an application of freezing point lowering by solute molecules that has considerable practical interest. The organic anti-

freeze chemicals of commerce are polar non-electrolytes possessing one or more hydroxyl groupings. Information on their antifreeze properties is still highly empirical, and the relative usefulness of any new substance that is

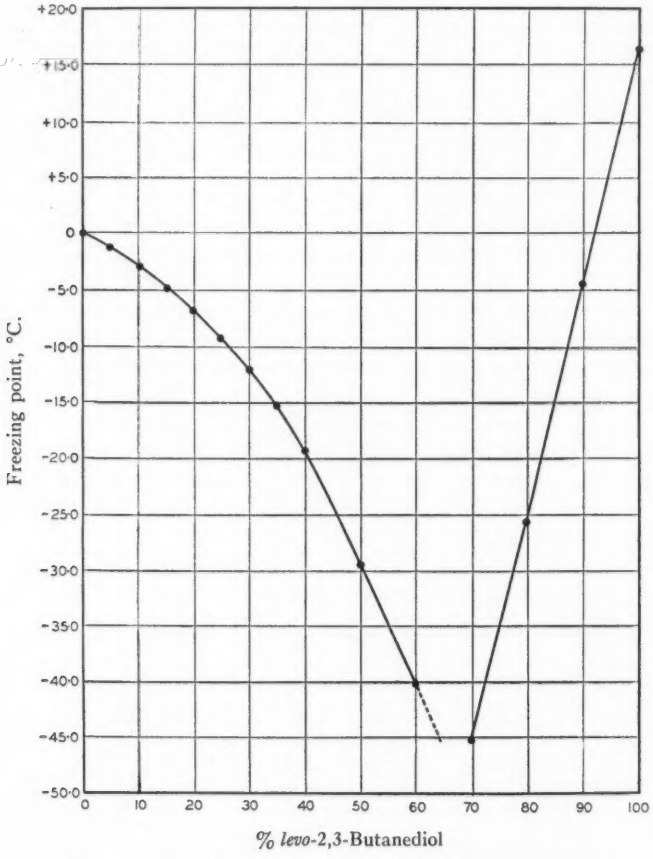

FIG. 1. *Freezing points of aqueous levo-2,3-butanediol solutions.*

proposed for this purpose cannot be predicted with any degree of accuracy. Raoult's law is known to apply only to "ideal" solutions, and divergences are to be expected in radiator solutions of low freezing point. Theoretical freezing point values calculated by its application to solutions of the commercial antifreeze compounds are presented in Table I, however, since they shed some light on the relative importance of molar freezing point lowering and contributing factors such as hydration.

Among the five antifreeze chemicals listed in Table I, a general relation exists between molecular weight and observed freezing point lowering;

methanol is the most effective and glycerol is the least at equivalent percentages by weight, and at most concentrations the remaining compounds take intermediate positions in the expected order. Between chemicals, the observed differences in freezing point are much smaller than would be expected from their molecular weights. Thus at 50% by weight, the calculated freezing point values for ethanol, ethylene glycol, and *levo*-2,3-butanediol are −40.4°, −30.0°, and −20.7° C., respectively, whereas the freezing point values actually were −37°, −35°, and −29.6° C. The freezing point lowering observed with *levo*-2,3-butanediol is approximately 4/3 the calculated value over the range 0 to 60% diol, and the same tendency is consistently shown by ethylene glycol and glycerol although to a lesser extent. Up to concentrations of 40%, the observed values for ethanol and methanol also exceed the calculated values slightly, but, at concentrations of 50% and higher, the observed freezing point depression is less than would be expected from similar calculations.

Jones and co-workers (16, 17) found that the hygroscopic salts crystallizing with the greatest amount of water produced the greatest molecular lowering of the freezing point, and they indicated the importance of hydration in many instances in which freezing point lowering was exceptionally great. Hydration of the solute is evidently responsible for the abnormally large depression of the freezing point of water by ethylene glycol, glycerol, and *levo*-2,3-butanediol, all three of which are strongly hygroscopic: part of the water is bound by residual valence forces to the polar solute, the hydrated molecules then acting as units in depressing the freezing point of the water that remains. Commercial antifreeze solutions and the cellular contents of frost- and drought-resistant plants evidently have more in common than has hitherto been realized. The present indication of the importance of hydration in the freezing point lowering shown by *levo*-2,3-butanediol is supported by viscosity data presented in this paper, as well as by densimetric and polarimetric observations that will be published elsewhere (5).

Existing information, which need not be reviewed here, indicates that hydration occurs in aqueous solutions of methyl and ethyl alcohols. The question arises as to why the freezing point lowering is not strongly promoted by hydration when these two chemicals are employed. At concentrations of 40% and lower, one molecule or less of water is bound by each alcohol molecule (16), i.e., the hydration tendency is much less marked than with ethylene glycol, glycerol, and *levo*-2,3-butanediol. Pairing of solute molecules may also be partly responsible for the fact that freezing point lowering with these two chemicals is not greater than it is (16). With alcohol concentrations of 50% and higher, the solid phase is evidently an alcohol hydrate, the freezing point being progressively lowered with rising alcohol concentration as a result of hydrate solubilization.

The relatively high freezing temperature of essentially pure *levo*-2,3-butanediol has practical significance. The freezing point of pure ethylene glycol is nearly 30° lower than that of *levo*-2,3-butanediol, and is reduced still further

by the presence of the water (usually 3%) and other substances that are present in the commercial product. To prevent solidification in the container prior to use, water or other substances could be added to *levo*-2,3-butanediol, 15 to 20% water giving ample protection to temperatures of −20° C.

The freezing point curve for aqueous solutions of *meso-dextro*-2,3-butanediol (Fig. 2) is characterized by the formation of a *meso*-hydrate that crystallizes at temperatures well above the freezing point of water, approaching that of the anhydrous diol mixture. The presence of the *dextro*-form leads to a general reduction of the freezing points, but the various aspects of the freezing-point–diol-concentration data arise from the changing nature of the solid phase, which is successively water, *meso*-hydrate, and anhydrous diol. Beginning at 0% diol (Fig. 2) the freezing point is depressed by the addition of the

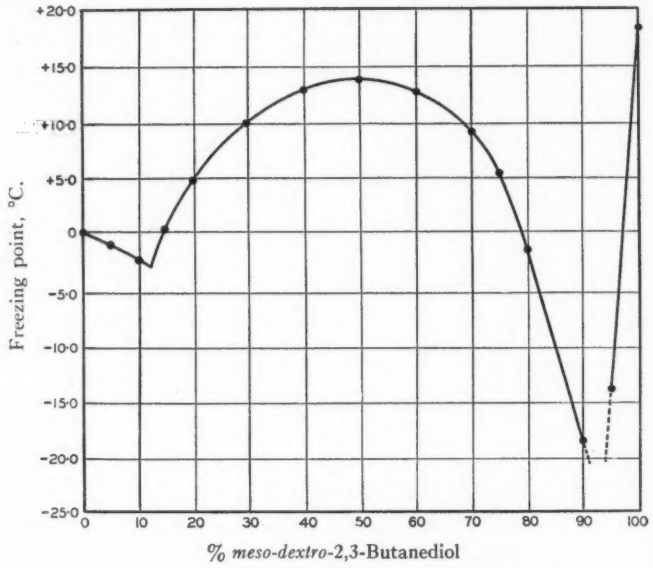

FIG. 2. *Freezing points of aqueous meso-dextro-2,3-butanediol solutions.*

diol mixture up to concentrations of 12%, the solid phase here being ice, there being sufficient water over this range of concentrations to keep the hydrate in solution at the equilibrium temperatures. The addition of further diol saturates the system with *meso*-hydrate which now becomes the solid phase, the freezing point of the mixture rising as the proportion of free or solvent water is reduced. The highest point on the freezing point curve represents maximum hydration, which is attained at 50% diol. With additional diol the freezing point of the *meso*-hydrate is depressed to a minimum, which is attained at 90% diol. Beyond this eutectic, the solid phase is

anhydrous diol, the freezing point rising sharply as the quantity of solvent hydrate is reduced. Sixty per cent aqueous solutions of the diol mixtures produced by *Aeromonas hydrophila* and *Bacillus subtilis* showed freezing points of +12.8° and +5.2° C., respectively, the freezing point value dropping as the proportion of *meso*-isomer is reduced. It should be noted that the present data are entirely at variance with the earlier statements made by Wilson and Lucas (36) on the freezing point characteristics of aqueous *meso*-2,3-butanediol solutions.

The high freezing temperature of aqueous *meso*-2,3-butanediol solutions has considerable bearing upon the practicability of employing the *levo*-isomer as an antifreeze. Contamination of *A. polymyxa* cultures with other butanediol-producing organisms could render the product useless as an antifreeze commodity. It is conceivable that races or variants of *A. polymyxa* exist that produce a mixture of isomers or could do so either by mutation or under special environmental conditions. In order to free the *levo*-form from esters, it is necessary to add alkalies before rectifying, with consequent possibilities of racemization. This contingency also exists in the automobile radiator, particularly under the mildly alkaline conditions that are often imposed to reduce the corrosion of metals by water. These potential sources of difficulty have been examined by the experiments that follow.

TABLE II

PHYSICAL PROPERTIES OF *levo*-2,3-BUTANEDIOL SAMPLES OBTAINED FROM DIFFERENT STRAINS OF *Aerobacillus polymyxa*

Organism	Alkali treatment*	Polarization value, 1 dm., at 25° C.	Freezing point, °C.	F.p. of 70% aqueous solution, °C.
C38 (2)	None	−12.60	+16.1	−42.8
C38 (2)	NaOH	−12.53	+16.1	−42.8
C42 (2)	None	−12.68	+16.1	−44.5
C8 (1)	$Ca(OH)_2$	−12.33	+15.7	−42.5
C4, 21, 25 (mixed strains)	None	−12.55	+16.0	−41.3
C4, 21, 25	$Ca(OH)_2$	−12.35	+15.5	−41.0
C4, 21, 25	NaOH	−12.45	+15.9	−42.2

* *Fermented wheat mash adjusted to pH 10.0–10.5 before filtration and diol recovery.*

The low optical rotation values of the diol samples referred to in Table II are attributed to the pronounced effect of small amounts of water on the optical rotatory power of this compound (5). Significant differences in freezing point lowering were not observed among butanediol samples obtained from different strains of *A. polymyxa*, regardless of whether they were or were not exposed to calcium hydroxide and sodium hydroxide in the recovery process (Table II). This observation has been borne out by subsequent experience, the products obtained with many different strains of *A. polymyxa* at the butanediol pilot plant having consistently shown the antifreeze characteristics

depicted in Fig. 1. While our experience does not entirely rule out the possible appearance of the *meso*-form in the *A. polymyxa* fermentation or in the subsequent stages of recovery, the chances for such an occurrence would now seem to be remote.

The influence of the *meso*-isomer on the freezing point of *levo*-2,3-butanediol solutions of uniform water content is illustrated by the experiment reported in Table III. At a water content of 40%, the freezing point is raised when the

TABLE III

EFFECT OF *meso*-2,3-BUTANEDIOL ON THE FREEZING POINT OF AQUEOUS *levo*-2,3-BUTANEDIOL SOLUTIONS HAVING WATER CONTENTS OF 40 AND 60%

Composition of diol	40% water	60% water
100% *levo*	−40.4° C.	−19.4° C.
95% *levo* 5% *meso*	−37.0	−21.0
90% *levo* 10% *meso*	−28.2	−21.0
85% *levo* 15% *meso*	−18.6	−17.2
80% *levo* 20% *meso*	−14.0	−12.4
50% *levo* 50% *meso*	+1.55	+1.55

meso-isomer is present to the extent of 5% of the total diol. The freezing point of solutions having water contents of 60% is actually lowered slightly by the presence of small amounts of the *meso*-form, but it rises quite sharply when this isomer makes up 15% or more of the total diol content.

The possibility of a *levo-meso* transformation in boiling aqueous solutions to which alkali had been added was examined by the experiment reported in Table IV. Adjustment of the pH of 50% aqueous solutions to values as high as 10.5 followed by 72 hours' refluxing did not result in the appearance of the *meso*-isomer, as judged by freezing point and optical rotatory power, both of these properties remaining substantially unchanged. The freezing point of

TABLE IV

OPTICAL ROTATORY POWER AND FREEZING POINT OF 50% *levo*-2,3-BUTANEDIOL SOLUTIONS AFTER 72 HR. REFLUXING TREATMENT

Initial pH	Optical rotation, 2 dm.	F.p. °C.
6.95	−8.53	−34
8.90	−8.38	−33
10.82	−8.38	−33

levo-2,3-butanediol solutions was also determined after use in the cooling systems of a fleet of light trucks throughout the winter of 1944–45, the diol concentration being estimated by reference to refractive index tables (5). The observed freezing points in all cases agreed with the values shown in Fig. 1 within $\pm 0.5°$ C. The driving tests were entirely satisfactory in so far as operation of the motors was concerned.

Viscosity

The rate of circulation and general effectiveness of radiator solutions as coolants at very low temperatures is largely governed by their viscosity. Since the viscosity coefficient increases quite regularly with rising boiling point within series of homologous liquids, the advantage of permanence or high boiling point offered by aqueous solutions of glycerol or ethylene glycol might be expected to entail a considerable increase in viscosity over that of ethanol or methanol solutions. With the exception of the data provided by Cummings (7) for solutions of commercial glycerine, Prestone, and denatured alcohol at temperatures down to $-8°$ C., the available viscosity data for organic antifreeze fluids are limited to temperatures of 0° C. and upwards, most of the measurements referring to temperatures of 20° C. and higher. The changes in viscosity with concentration and temperature are very pronounced with both the non-volatile and volatile chemicals but there the resemblance stops. Addition of water to ethylene glycol or glycerol reduces the viscosity coefficient very drastically, evidently as a result of diminished association between like molecules. Addition of water to ethanol or methanol results in a very pronounced increase, evidently as a result of solvent–solute association. At 0° C. the viscosity of 40% ethanol is roughly four times that of either pure component and is approximately the same as that of 40% ethylene glycol at the same temperature, notwithstanding the fact that pure ethylene glycol is 17 times more viscous than ethanol at 20° C. (13). From the broad indications that are provided by existing data at high temperatures and experience gained in freezing point determinations, the order of increasing viscosity for liquid compositions freezing in the temperature range $-30°$ to $-50°$ C. is apparently methanol, ethanol, ethylene glycol, and glycerol, the viscosity of the glycerol solutions being much higher than that of the remaining three. Between ethylene glycol, methanol, and ethanol solutions the differences in viscosity are probably not large enough to be of practical importance.

The literature contains no information as to permissible viscosities for radiator solutions at low temperatures. In the absence of suitable standards, a viscosity of 500 centistokes has been selected as representing a level at which the initial circulation rate would not be retarded to an objectionable extent, and of 1000 centistokes as the upper limit beyond which circulation would be seriously impeded. From the flow properties observed in the course of freezing point determinations, Olsen *et al.* (25) concluded that 58% gylcerol would circulate in the radiator system at $-42°$ C. Our observations on the viscosity

of glycerol solutions (Fig. 4) indicate a viscosity value of around 1500 centistokes at this concentration and temperature, which is half as high again as the limiting value selected for our purposes.

The effect of water content on the absolute viscosity at 20° C. of glycerol, *meso-dextro*-2,3-butanediol, *levo*-2,3-butanediol, and ethylene glycol solutions is shown in Fig. 3. Past work on the viscosity of liquids (13) has established general relations between molecular structure and flow properties that have

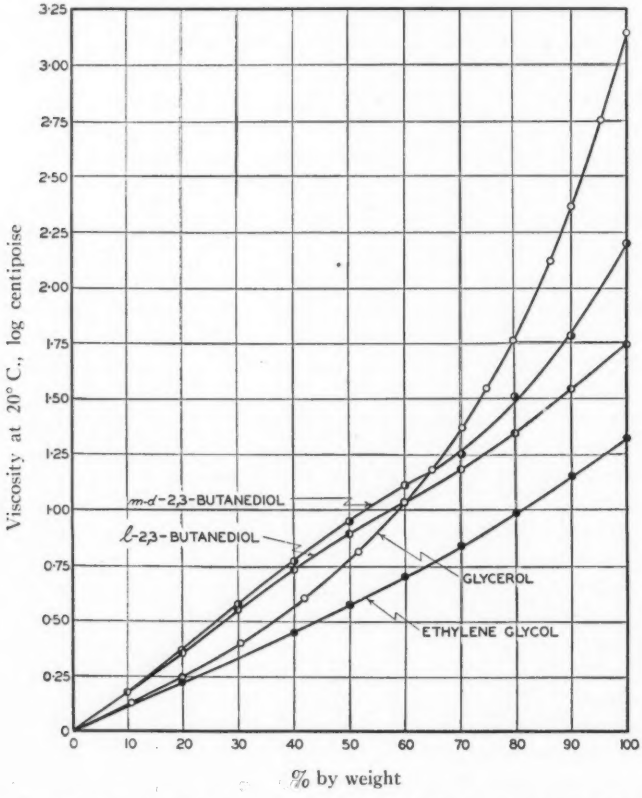

FIG. 3. *Absolute viscosity of aqueous solutions of ethylene glycol, levo-2,3-butanediol, meso-dextro-2,3-butanediol, and glycerol at 20° C. Data for glycerol are taken from tables published by M. S. Sheely (29).*

an immediate bearing on the very marked dissimilarities reported in this figure: hydroxyl groupings lead to association of like molecules in pure liquids and to hydrate formation in aqueous solutions; additional CH_3 groupings on otherwise similar molecules raise the viscosity coefficient by an amount that can be predicted by the use of equations; and differences in the viscosity of liquid stereoisomers are caused by differences in free space, the isomer

having the higher viscosity also having the higher density. Among the anhydrous liquids (Fig. 3), ethylene glycol has the lowest viscosity. This liquid is known to be highly associated in the absence of water (13). The 2,3-butanediols show higher values; this is to be expected in view of the two additional CH_3 groupings. The *meso*-form is more viscous and also has a higher density than the *levo*-form. This accords with the free space concept. The very high viscosity of anhydrous glycerol, i.e., 1499 centipoises at 20° C. (29), arises from its pronounced association and low free space. In an extensive study of the volume–temperature–pressure relations of liquid hydrocarbons, alcohols, glycols, and glycerol, Bridgman (3) found that, of all compounds tested, glycerol had the lowest compressibility. Some indication of the differences between pure *levo*-2,3-butanediol and glycerol in this respect is provided by their densities, which stand in the ratio of 0.99 to 1.26.

The sagged form of the viscosity–concentration curves for ethylene glycol and glycerol solutions (Fig. 3) indicates that dissociation resulting from admixture of highly associated liquids has a predominant influence on their fluidities, obscuring the effects of hydration, which occurs in both these systems. The outstanding feature of the curves for the 2,3-butanediols (Fig. 3) is their convexity at water contents of 20% and higher, the behaviour of both isomers being substantially similar. For this there appears to be but one possible explanation: within the indicated range of concentrations, the effects of dissociation are counterbalanced by hydration, the latter tending to increase the viscosity. Judging from the viscosity data, the *levo*- and *meso*-isomers are both characterized by a strong affinity for water; the remarkable differences in their antifreeze characteristics result from their differing solubilities in the hydrated state. Because of accompanying hydration, 2,3-butanediol solutions at concentrations of 50% or less are more viscous than glycerol solutions of corresponding concentration. Thus while hydration improves the antifreeze characteristics of the *levo*-isomer from the standpoint of freezing point lowering, the accompanying effect on viscosity largely offsets this advantage.

Fig. 4 presents comparative kinematic viscosity data for 60% solutions of *levo*-2,3-butanediol, glycerol, and ethylene glycol over the temperature range +20° C. to −40° C. The butanediol solution is more viscous than that of glycerol at low temperatures, this difference becoming quite pronounced at −30° C. to −40° C. The viscosity of the ethylene glycol solution is much lower, the present data indicating that a value of 500 centistokes would be attained only at temperatures below −50° C. This viscosity value is shown by 60% glycerol at −33° C., and by 60% *levo*-2,3-butanediol at −25.5° C. (Table V). A value of 1000 centistokes is attained by 60% glycerol at −39° C. and by 60% *levo*-2,3-butanediol at −30° C. When both freezing point lowering and viscosity are taken into consideration, 50% *levo*-2,3-butanediol appears most suitable for general use (Table V).

The decrease in viscosity that accompanies rising temperature is much more pronounced with organic antifreeze solutions than with pure water, the differences in fluidity between solution and pure solvent becoming negligible

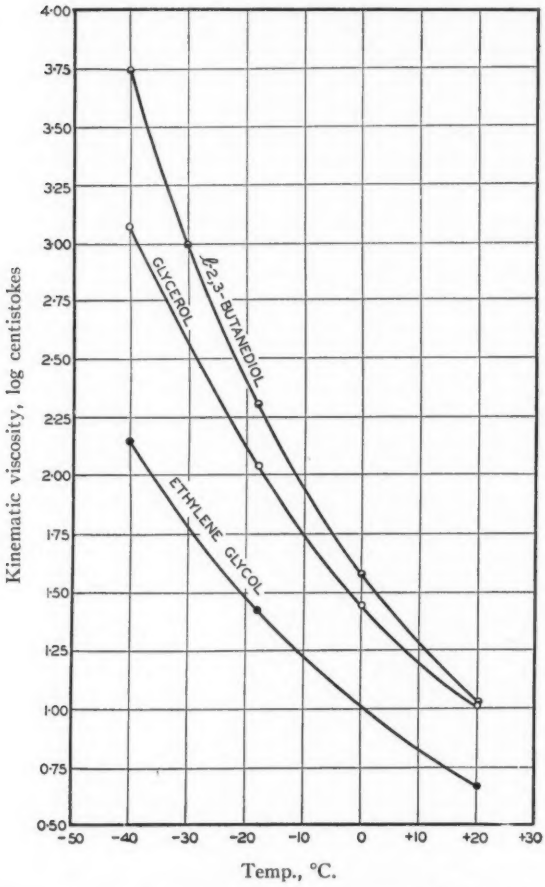

FIG. 4. *Kinematic viscosity of 60% levo-2,3-butanediol, glycerol, and ethylene glycol solutions at low temperatures.*

TABLE V

TEMPERATURES AT WHICH VISCOSITY VALUES OF 500 AND 1000 CENTISTOKES ARE ATTAINED BY AQUEOUS SOLUTIONS OF *levo*-2,3-BUTANEDIOL

levo-2,3-Butanediol, %	Temperature, °C.	
	500 centistokes	1000 centistokes
80	−18	−24
70	−22	−27
60	−26	−30
50	−29	−34

in so far as engine performance is concerned after a few minutes' operation of the motor. The converse is true of inorganic antifreeze solutions (13); with these the relative viscosity, referred to that of water at the same temperature, increases to a quite pronounced extent with rising temperature. Fig. 5 demonstrates the changes in viscosity of aqueous *levo*-2,3,-butanediol solutions

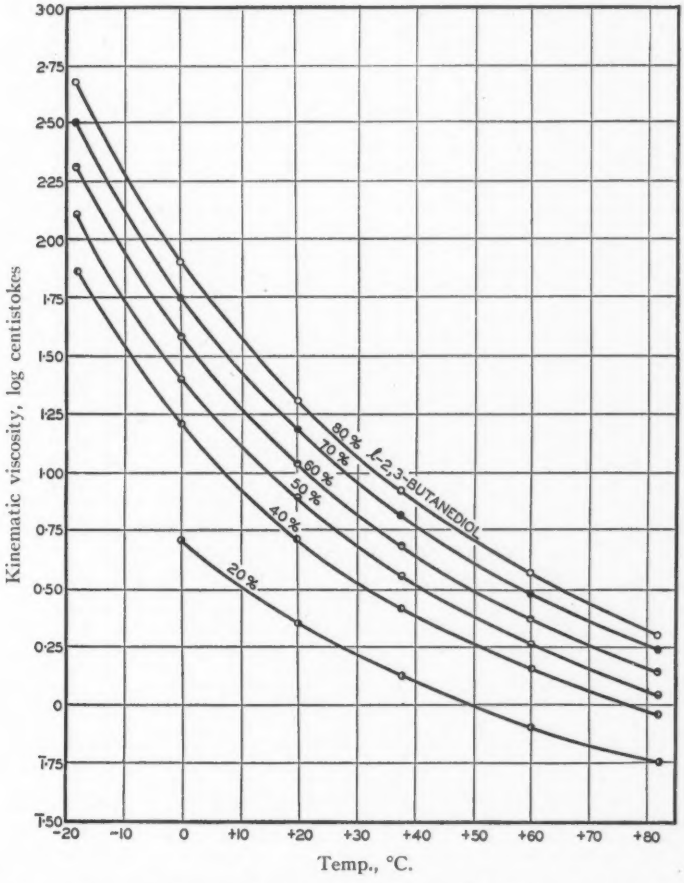

FIG. 5. *Kinematic viscosity of aqueous levo-2,3-butanediol solutions, expressed logarithmically, as a function of concentration and temperature.*

that occur when the temperature is increased from −20° C. to +82° C., this temperature range including the usual radiator temperatures during winter driving (+60° to +71° C.) as well as the temperature normally attained immediately after the motor is shut off (+82° C.). Fig. 6 illustrates the effects of diol concentration and temperature over a more limited range, the data

being presented in this figure as kinematic viscosity units for purposes of convenient reference.

Heat Capacity

Since automobile cooling systems are designed for water, high specific heats are desirable in antifreeze solutions. Information on the specific heat of 2,3-butanediols is at present limited to that provided by Khokhlovkin and

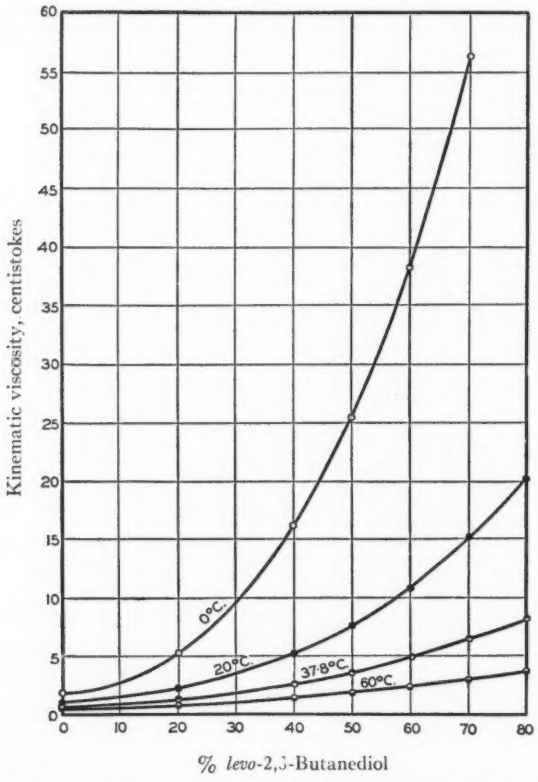

FIG. 6. *Kinematic viscosity of aqueous levo-2,3-butanediol solutions in relation to concentration and temperature.*

Kalacheva (19). The butanediol values given in Table VI were obtained from this source, that of the aqueous solution being only a rough estimate. Values for the remaining antifreeze chemicals in this table were calculated using data obtained from other sources (15, 24, 31).

From the comparative data presented in Table VI, it is apparent that butanediol does not differ greatly from ethylene glycol or glycerol with respect to specific heat, and that solutions of ethanol and methanol at concentrations

of 50% by weight have a specific heat much closer to that of water than similar concentrations of butanediol, ethylene glycol, and glycerol. Cummings (7) has pointed out that heat capacity per unit volume is more useful as an

TABLE VI

SPECIFIC HEATS OF ANTIFREEZE CHEMICALS AT 30° C.

	Anhydrous	50% by wt. aqueous solution
Methyl alcohol	0.61	0.91
Ethyl alcohol	0.59	0.93
Ethylene glycol	0.58	0.80
Glycerol	0.575	0.78
2,3-Butanediol	0.60	0.80

index of antifreeze cooling properties, and, on this basis, the discrepancy between the non-volatile and volatile chemicals would be considerably reduced. Judging from engine dynamometer tests reported by Green, Lamprey, and Sommer (12), engine performance actually is not altered significantly when solutions of ethylene glycol, ethanol or methanol are substituted for water as the cooling agent.

Surface Tension

Knowledge of the surface tension of antifreeze solutions provides information on their creeping and foaming tendencies. Liquids of low surface tension have a greater tendency to escape through small crevices in the cooling system than water, and as a general rule their solutions have a stronger foaming tendency (10). Untreated ethylene glycol solutions have already been shown by empirical test to leak more readily than water (12). The surface tension of pure *levo*-2,3-butanediol (Fig. 7) is considerably lower than that of ethylene glycol. This is to be expected from Traube's rule, the surface tension generally tending to drop off with increasing molecular weight among related chemicals. The shape of the butanediol graph conforms with that generally shown by aqueous solutions of capillary-active substances, a low concentration causing a pronounced lowering of the surface tension, intermediate and high concentrations reducing the value gradually to that of the pure liquid (10). From Gibbs rule, *levo*-2,3-butanediol should have a greater tendency to concentrate at the liquid–air interface than ethylene glycol.

Agents are customarily added to ethylene glycol solutions to reduce foaming and seepage during service (12). The present data indicate that similar precautions may be desirable when *levo*-2,3-butanediol is employed, although it is yet too early to assess the practical importance of the differences reported in the accompanying figure.

Corrosion

Methanol and glycerol were at first marketed for use in automobile radiators in very impure form, the free acids and electrolytes that they contained serving

to promote corrosion. This fault was soon corrected but the popular impression has persisted that antifreeze chemicals stimulate corrosion and that corrosion inhibitors are necessary adjuncts. A host of corrosion inhibitors

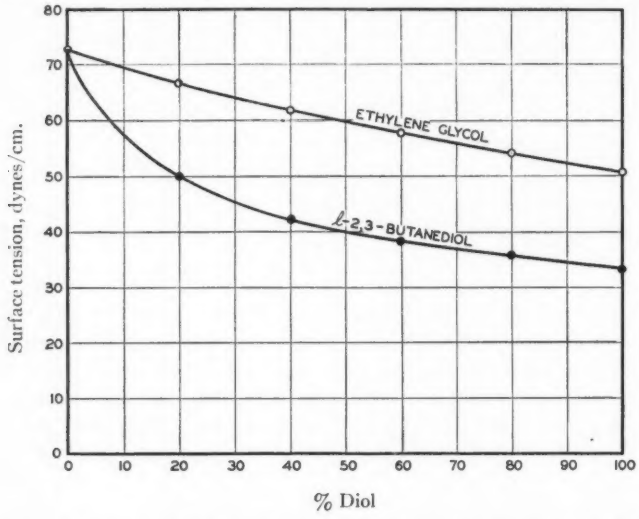

FIG. 7. *Surface tension of aqueous solutions of levo-2,3-butanediol and ethylene glycol at 25° C.*

has been patented for use in organic antifreeze solutions (33), but published information on this subject (7, 8, 18, 26, 37) shows agreement in indicating that water alone is at least as corrosive as aqueous solutions of the common organic antifreeze chemicals.

TABLE VII

CORROSION OF STEEL PANELS BY TWO MONTHS' TOTAL IMMERSION IN AQUEOUS ANTIFREEZE SOLUTIONS

Sample	Weight loss, gm./sq. in.
50% *levo*-2,3-butanediol	0.0122
50% *levo*-2,3-butanediol containing 0.1% $NaNO_2$	None
50% ethylene glycol	0.0190
50% "Prestone"	0.0002

Table VII reports a comparison of the corrosive action on steel of aqueous solutions of *levo*-2,3-butanediol and ethylene glycol with and without nitrite inhibitor. In the absence of nitrite, the steel panels were attacked by both solutions to an approximately equivalent extent. In the presence of 0.1% sodium nitrite the corrosion of steel by aqueous *levo*-2,3-butanediol was

eliminated, as was also the case with commercial ethylene glycol solution containing the inhibitor or inhibitors customarily added.

Table VIII reports an experiment in which test plates of steel, brass, aluminum, and lead were bolted together and then immersed for two months in 50% *levo*-2,3-butanediol solution containing 0.1% sodium nitrite. The attack

TABLE VIII

CORROSION OF STEEL, BRASS, ALUMINUM, AND LEAD BY 50% *levo*-2,3-BUTANEDIOL CONTAINING 0.1% SODIUM NITRITE (PANELS BOLTED TOGETHER DURING TWO MONTHS' IMMERSION)

Panel	Weight before test, gm.	Weight after test, gm.	Weight change	Weight change, gm./sq. in.
Steel	13.3072	13.3066	−0.0006	−0.0001
Brass	15.7191	15.7235	+0.0044	+0.0009
Aluminum	4.9495	4.9528	+0.0033	+0.0007
Lead	27.7316	27.1652	−0.5664	−0.1135

on steel, brass, and aluminum is judged of no practical importance. Lead was very strongly attacked, and subsequent tests showed that this arose from the use of distilled water in making up the solutions. Ethylene glycol solutions made up in the same way cause quite as much damage. The corrosive action of pure water on lead has been satisfactorily explained by Thresh (32, 33) and is also discussed by Evans (9, p. 98): in the absence of sulphates or bicarbonates the lead passes freely into solution, whereas in ordinary tap water an impervious protective film of lead sulphate or carbonate is formed over the exposed surface. Cummings (7) has suggested the use of soft water in radiators as a means of reducing scale formation. It should be noted that this practice might lead to a greater corrosion of soldered joints than occurs when tap water is employed.

If special precautions are not taken, *levo*-2,3-butanediol is contaminated with esterified acetic acid in the course of its recovery from fermented mashes. In the foregoing corrosion experiments, the ester content of the diol was 1.0%, expressed as monoacetate, and from the present results this concentration appears to be permissible. Since the acetate is partially hydrolysed in the presence of water, the ester content should be kept as low as possible in butanediol intended for use as an antifreeze.

Solvent Action on Automobile Finishes

Ethanol and methanol have a strongly deteriorative effect on the protective coatings of the engine hood (7), but this property has been claimed to be unimportant when the alcohols are considerably diluted with water (8). Since objection to ethylene glycol has never been taken in this respect, its deteriorative action on typical automobile finishes (nitrocellulose lacquer, "Dulux", and alkyd base enamels) has been compared with that of *levo*-2,3-butanediol (Table IX). All three finishes were softened to some extent by

TABLE IX

SOLVENT ACTION OF *levo*-2,3-BUTANEDIOL AND ETHYLENE GLYCOL ON AUTOMOBILE FINISHES

Metal finish	*levo*-2,3-Butanediol		Ethylene glycol	
	60%	100%	60%	100%
Nitrocellulose lacquer	2	3	2	2
"Dulux" enamel C.I.L.	3	2	3	2
Alkyd base enamel	4	4	3	3

Rating of the physical condition of metal finishes after exposure: 1—good, 2—fair, 3—poor, 4—bad.

exposure to these antifreeze compounds, water content having little effect over the tested range of concentrations. Ethylene glycol tended to be slightly less deteriorative than *levo*-2,3-butanediol, but the observed differences in this respect are not judged large enough to have practical significance. The results indicate (Table IX) that precautions should always be taken to prevent exposure of automobile finishes to antifreeze compounds of this type, and that alkyd base enamels are more easily damaged in this way than nitrocellulose lacquers.

Effects on Natural and Synthetic Rubber

One of the most objectionable characteristics of oils and kerosene as engine coolants is their strongly deteriorative action on rubber hose connections (7, 18, 37), the same being generally true of oil-type corrosion inhibitors (12). Technical data are lacking on the relative suitability of aqueous antifreeze solutions in this respect. Green *et al.* (12) conclude that hose failures are primarily related to the grade of rubber and type of hose employed, rather than to the type of aqueous antifreeze solution that is used in the cooling system. They report that radiator hose connections remain serviceable for a longer time with commercial ethylene glycol solutions than with water. This is somewhat at variance with the statement of Keyes (18), who cited rubber-softening as a disadvantageous characteristic of ethylene glycol.

Table X reports the changes in various properties of natural and synthetic rubber that resulted from three days' immersion in 60% *levo*-2,3-butanediol and ethylene glycol solutions at 80° C. The change in tensile strength was approximately the same with both antifreeze solutions, Buna S being affected to a greater extent. The "elongation at break" test on both rubber compounds indicated a slight superiority for the butanediol solution. Neither solution reduced the hardness of Buna S appreciably, and the hardness of natural rubber was affected only to a small extent by the butanediol solution. The butanediol solution had a considerably greater swelling action on both types of rubber. According to T. R. Griffith of the National Research Council rubber laboratory, a 20% volume increase would not materially affect the serviceability of rubber hose connections, and in his opinion the observed

TABLE X

EFFECT OF 60% ETHYLENE GLYCOL AND 60% *levo*-2,3-BUTANEDIOL ON NATURAL AND BUNA S RUBBER COMPOUNDS (THREE DAYS' IMMERSION AT 80° C.)

	Tensile strength (lb./sq. in.)	Elongation at break, %	Volume change, %	Hardness number
Natural rubber				
Untreated	3075	645	0	51
Ethylene glycol	2800	595	+ 1.5	49
levo-2,3-Butanediol	2820	635	+11.9	46
Buna S rubber				
Untreated	2850	615	0	56
Ethylene glycol	2000	375	+ 5.9	54
levo-2,3-Butanediol	2070	410	+10.7	54

differences in swelling action do not detract from the usefulness of *levo*-2,3-butanediol as an antifreeze compound.

Permanence

Fig. 8 demonstrates that the boiling points of aqueous *levo*-2,3-butanediol solutions are essentially the same as those of ethylene glycol and glycerol of equivalent concentrations. Barring losses by leakage and by overflow after

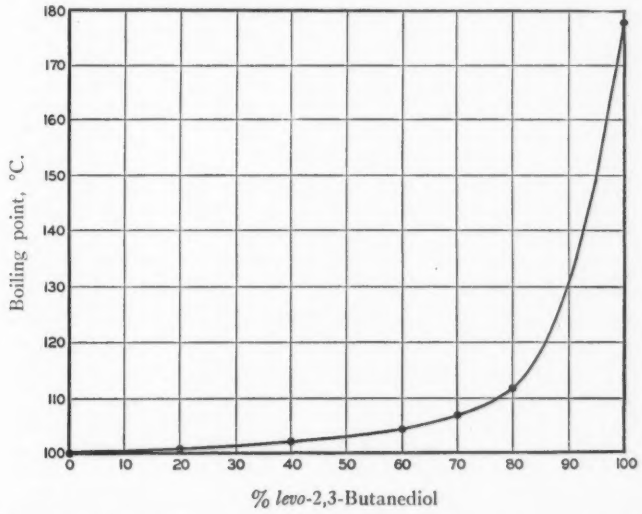

FIG. 8. *Boiling points of aqueous levo-2,3-butanediol solutions at atmospheric pressure.*

the motor is shut off, only water need be added to maintain a uniform diol concentration. As with other permanent-type antifreeze compounds, the solution could be saved for re-use.

Inflammability

The inflammability of ethanol and methanol imposes a fire hazard, the open-cup flash points of the pure chemicals being below room temperature (15° to 16° C.), while that of fairly concentrated aqueous solutions is well below usual radiator temperatures. The open-cup flash point of *levo*-2,3-butanediol is 110° C., which is similar to the value that has been reported elsewhere (2) for ethylene glycol (116° C.). With either of the last two substances the presence of small amounts of water would increase the flash point very considerably.

Solubility

The solubility–temperature relations for aqueous *levo*-2,3-butanediol solutions containing various third components will be treated in detail in a forthcoming publication (6). The present chemical is miscible in all proportions with any of the common antifreeze chemicals, their antifreeze properties in admixture being approximately additive.

Expansion on Solidification

The freezing point of organic antifreeze solutions is the highest temperature at which crystals can be induced to separate on seeding. As the temperature is lowered further, the liquid becomes "mushy", but the small accompanying expansion due to ice formation is of no practical consequence since the system is still semifluid. The importance of expansion when the solution becomes solid has been tested by filling Erlenmeyer-shaped weighing bottles, having thin glass walls, with 40% *levo*-2,3-butanediol and ethylene glycol solutions and solidifying the contents at temperatures 20° C. below their freezing points. The fact that the glass vessels did not rupture demonstrated that solidification of these solutions in the radiator would not lead to damage by expansion.

Thermal Expansion

A low coefficient of thermal expansion is desirable in antifreeze fluids (18, 37), and in this respect *levo*-2,3-butanediol and its solutions compare favourably with ethylene glycol. Using the simplified expression $V_t = V_0 (1 + \alpha t)$, comparable values for $\alpha \times 10^3$ over the temperature range 20° to 40° C. are: water, 0.3; 60% *levo*-2,3-butanediol, 0.79; *levo*-2,3-butanediol, 0.85; 60% ethylene glycol, 1.15; anhydrous ethylene glycol, 0.90; ethyl alcohol, 1.15. The specific gravity data on which the *levo*-2,3-butanediol figures are based are presented elsewhere (5).

Density

The density of antifreeze solutions is of interest for two reasons: with comparatively heavy liquids such as glycerol, the antifreeze chemical sinks to the bottom of the radiator if it is not mixed with water beforehand; because of

the ease with which it may be measured, this property also forms the basis of practical tests for freezing point protection in used radiator solutions, ethylene glycol and glycerol solutions being much heavier, and alcohol solutions much lighter than water. From a practical standpoint it is impossible to determine the strength of *levo*-2,3-butanediol solutions by density measurements since the values for its solutions are very close to that of water at all concentrations.

Conclusions

levo-2,3-Butanediol and ethylene glycol are judged equally satisfactory as antifreeze compounds from the standpoints of stability, permanence, heat capacity, inflammability, thermal expansion, expansion on solidification, and deteriorative action on metals, metal finishes, and rubber hose connections. Admittedly, there are some differences in these respects, but on the whole they are judged too small to be of practical importance in the present application. Ethylene glycol solutions have higher surface tensions and lower freezing points than the corresponding *levo*-2,3-butanediol solutions. The differences observed in these two properties are considered to be of secondary importance in view of the relative ease with which creeping and air-entrainment tendencies may be controlled and the fact that temperatures below $-40°$ C. are seldom encountered.

The detrimental properties of *levo*- 2,3-butanediol solutions are high viscosity at low temperature and uniform density at all concentrations. It is considered unlikely tha difficulties would arise from high viscosity except at temperatures below $-30°$ C. It should be noted that *levo*-2,3-butanediol solutions are rendered considerably less viscous by the addition of third components, and may then be used at a temperature of $-50°$ C. (6). The problem of testing butanediol solutions after use for diol concentration has been satisfactorily solved by co-workers who have devised and calibrated a practical instrument suitable for use in service stations.

The most suitable concentration for use in automobile radiators is judged to be 50%, and this strength has proved satisfactory in large scale driving tests. It may prove advantageous to add anticreep and antifoam agents although no need for them has been indicated so far in driving tests. Corrosion inhibitors such as sodium nitrite might also be added if there is greater need for rust inhibitors during the winter months than during the remaining seasons when water alone is used.

The future of *levo*-2,3-butanediol as an antifreeze rests with production costs and concurrent prices of competitive chemicals. According to Callahan (4), the *meso*-isomer made by fermentation of corn or wheat with *Aerobacter aerogenes* could probably compete successfully as a source of butadiene with ethyl alcohol obtained from the same raw materials: the yields of alcohol and of the *meso*-isomer are of the same order, and the higher yields of butadiene that are obtained with the diol would largely compensate for the higher cost of recovering the diol from fermented mashes. Existing information on the production of *levo*-2,3-butanediol with *Aerobacillus polymyxa* is largely restricted

to the use of buffered grain mashes as substrate, the yield of diol in this instance being lower than in the *Aerobacter aerogenes* fermentation. Although the *levo*-isomer could not be made as cheaply as ethyl alcohol or the *meso*-form, it could probably be marketed at a retail price considerably below the average price of ethylene glycol over the past 10 years. If the price of ethylene glycol was reduced greatly, *levo*-2,3-butanediol could remain in a competitive position only through technological improvements and adaptation of the process to cheaper raw materials. The antifreeze trade offers a considerable outlet for chemicals derived from plant products, but its limitations must be recognized. Judging from the volume of pre-war trade in antifreeze chemicals, the entire Canadian demand could be satisfied by a butanediol industry having an annual capacity of one, or at most two, million bushels of wheat.

Acknowledgments

This investigation was greatly facilitated by the assistance and co-operation of staff members of the Divisions of Applied Biology, Chemistry, and Mechanical Engineering. Dr. W. H. Cook, Director, Division of Applied Biology, suggested that the present study be undertaken and made numerous helpful suggestions. Mr. D. E. Wright provided extensive technical assistance in the experimental work and prepared the figures. Messrs. Dyson Rose and J. F. MacDonald prepared the *levo*-2,3-butanediol samples for the present studies, and Mr. J. D. Leslie supervised the winter driving tests to which reference is made. Our thanks are extended to Mr. A. C. Halferdahl and Miss K. Migurska, of the Division of Chemistry, who were responsible for the corrosion studies; to Messrs. T. R. Griffith, E. B. Storey, and Miss L. M. Ellement, who carried out the experiments on rubber deterioration; and to Mr. Glynn Michael, who conducted the reported tests on metal finishes. We are particularly indebted to Dr. J. W. Broughton and Messrs. B. I. Patterson and J. W. Black, of the Division of Mechanical Engineering, who were responsible for the viscosity and flash point determinations.

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THE PROBLEM OF HEAT ADDITION IN DUCTS[1]

By D. G. Samaras[2]

Abstract

The one-dimensional problem of heat addition in a duct with friction losses is examined.

The variation of the total head temperature and pressure ratio, as well as the static ones, have been obtained as functions of the Mach number and the frictional coefficient. It is shown that an extreme value of the total head temperature and pressure ratio is obtained when the Mach number equals unity. An extreme value of the static temperature is obtained at Mach numbers smaller or larger than unity, depending on the form of the duct.

It is concluded that when the total head pressure losses are to be kept low, a diverging duct must be used. The frictional losses have a convergence effect on the flow. When the friction losses are disregarded, no total head pressure loss will result if the area variation of the duct is such as to ensure a constant Mach number.

The results and conclusions found may be useful in the design of combustion chambers for gas turbines, propulsive ducts, and rockets.

Notation

The following symbols have been used in the analysis:

A = Cross-sectional area,
C_f = Friction coefficient,
g = Gravitational constant,
K = Constant,
ln = Naperian logarithm,
M = Mach number,
m = Exponent of the cross-sectional area variation,
p = Absolute pressure,
Q = Air mass-flow,
R = Radius of the cylindrical duct,
r = Radius of the cross-section (general case),
R_c = Gas constant,
Rel = Refers to relative values of the appropriate quantities, usually to values at the inlet of the duct,
T = Absolute temperature,
V = Velocity,
x = Axial co-ordinate,
y = Temperature ratio,
Z = M^2 = square of the Mach number,
α = Auxiliary function of the cross-sectional variation and friction, used for convenience only,
γ = Isentropic exponent,

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θ = Slope of the meridian of the duct wall,
ρ = Density,
τ = Shear stress (friction),
ω = Auxiliary function of the rate of heat addition and friction in the cylindrical duct.

The following subscripts have been employed:

$_{1,2,}$ = Inlet and outlet of the duct respectively,
$_{ex}$ = Extreme value,
$_{s}$ = For static,
$_{t}$ = For total head.

1.0 Introduction

The maximum attainable temperature by heat addition in a duct has often been questioned. The simplified problem of a cylindrical duct with no losses was examined, and several conclusions in divergence with present day experience were drawn. That led the author, two years ago, to attempt a general solution of the problem. It is well known that heat addition in a gas stream results in an increase of the static temperature and in an increase of the velocity, both changes being reflected in the variation of the total head temperature.

From the above it is reasonable to deduce that, in a gas-stream, heat can be added without necessarily increasing the static temperature; also a maximum static temperature can be reached and still further heat can be added with decreasing static temperature, by accelerating the fluid, until the gas velocity at a certain section reaches the local velocity of sound, and "choking" is said to occur.

According to the above and in order to avoid the misleading influence of the static temperature, the total head temperature has been employed, since it gives a true picture of the process of heat addition; also for comparative reasons the static temperature variation has been included.

The general problem of designing a duct of given inlet and outlet temperatures and loss distribution is a very complicated one; it is a three-dimensional problem and it is reduced to a two-dimensional one in the case of axial symmetry. Still, the two-dimensional problem is so complicated that no attempt was made to attack it, as the general conclusions drawn from the one-dimensional problem can be applied to that with slight modifications.

In the present stage of development very little is known of the reaction mechanism of combustion of technological fuels; therefore a theoretical calculation of the combustion process is more or less impossible. Even in the case of simple fuels such as methane, the process of combustion is a very complicated one. It was found that during the combustion of methane several intermediate products are formed, such as methyl alcohol and formaldehyde; also CC— and CH— bands have been spectroscopically observed.

For many fuels the reaction process is fundamentally different at different temperatures; at low temperatures cool flames may appear that are entirely

absent at higher temperatures. To this may be added the possibility of a time dependence of the chain reactions. From the above-mentioned multiplicity of the combustion phenomena, two idealized cases of the reaction process can be distinguished; that is, the thermal reaction and the chain reaction. In both cases a large increase of the reaction velocity appears with the time; in the first by the increase of the temperature due to the liberated heat, and in the second owing to chain branching. In practice we have a combination of both.

In spite of the complicated combustion phenomena, some empirical formulae can be established that may render immense help to the designer, by simplifying the treatment of the combustion process. In a homogeneous gas mixture the mass rate of combustion is proportional to the concentrations of the gases taking part in the reaction and to a reaction velocity given by the well known Arrhenius formula. This formula can also be deduced from statistical considerations by using Boltzmann's distribution law.

Not only physico-chemical but also aerodynamical phenomena are present in the combustion in a duct and these make the problem even more complicated.

It was found that the flame velocity of a Bunsen burner in the laminar region is considerably lower than in the turbulent region. Now considering that in a duct a great amount of turbulence is to be expected, the results on the flame propagation are obvious.

In a duct, two types of turbulence are usually present; the small and large scale turbulence. Large scale turbulence in a duct is usually produced by the wakes of bodies, especially in the case of the Kármán vortex trails. Small scale turbulence is produced in a combustion chamber of a gas turbine engine by the compressor wakes and in a propulsive duct by the entry oblique shock-waves.

It can be concluded that the rate of heat addition in an actual duct as a function of the geometrical co-ordinates is unknown, and the most simplified assumptions of flame propagation and ignition lag would not contribute very much to the conclusions drawn. Therefore the geometrical co-ordinates were disregarded and instead the mean Mach number across the section has been employed.

Finally, the best geometrical form of a duct may be found by combining the conclusions of the analysis with experimental evidence.

2.0 Assumptions

As was mentioned above, necessary simplifying assumptions were made in order to evolve the general equations in as simple form as possible.

Although the velocity, temperature, and pressure variation at any section is considerable and variable with time, their mean values have been used in the analysis.

The increase of the mass flow due to fuel addition has been neglected. A mean specific heat, constant for all cases, has been assumed. A mean shear stress, corresponding to the total frictional loss, has been assumed as applied parallel to the wall of the duct. In reality, owing to turbulence the losses are distributed throughout the volume of the duct; but a spatial distribution would only complicate matters.

A circular duct has been assumed; but as the form of the cross-section enters only in the frictional term, by taking into consideration the former assumption the results can be applied to any form of cross-section where the friction losses are small.

It was found in the analysis that the cross-sectional area that corresponds to a constant Mach number is an exponential function of the total head temperature ratio. This led us to the very useful assumption, that the cross-sectional area is an exponential function of the total head temperature ratio

3.1.0 General Equations of Motion

From Fig. 1 it can easily be seen that the equation of momentum in the axial direction is as follows:

$$d\left\{(p_s + \rho_s V^2)A\right\} - p_s dA + \tau . 2\pi r dx = 0 \tag{1}$$

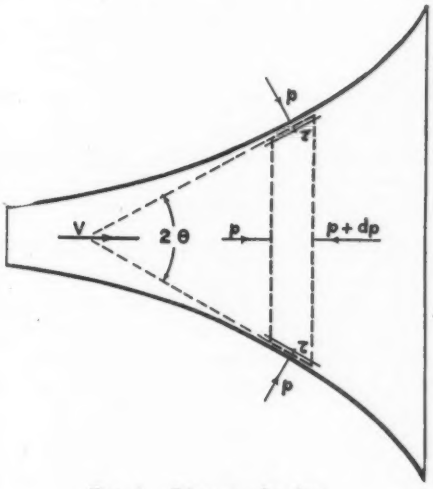

FIG. 1. *Diagram of a duct.*

The shear stress (friction) can be put in the form:

$$\tau = \tfrac{1}{2} C_f \rho_s \left(\frac{V}{\cos\theta}\right)^2. \tag{2}$$

The equation of continuity may be written as follows:

$$Q = g\rho_s V.A. \tag{3}$$

The equation of state for perfect gases may be written in the form:

$$p_s = g\rho_s R_c T_s . \tag{4}$$

The section area variation has been assumed as:

$$A = \pi r^2 = K y_t^m . \tag{5}$$

Now calling

$$Z = M^2 , \frac{T_t}{T_{t1}} = y_t , \text{ then } V^2 = g\gamma R_c \frac{Z \cdot T_t}{1 + \frac{\gamma - 1}{2} Z} .$$

3.2.0 The Equation of the Total Head Temperature Ratio

From the above equations the following can be obtained:

$$d\left\{\rho_s V^2 A \left(1 + \frac{1}{\gamma Z}\right)\right\} - p_s dA + \tfrac{1}{2} C_f \rho_s \left(\frac{V}{\cos\theta}\right)^2 2\pi r dx = 0, \tag{6}$$

and finally, after some simple transformations as shown in Appendix I, we obtain

$$\frac{1 - Z}{Z\left(1 + \frac{\gamma - 1}{2} Z\right)} \cdot \frac{dZ}{dy_t} + 2\left(1 - \frac{\gamma C_f}{\sin 2\theta} Z\right) \frac{d \ln A}{dy_t} = \frac{1 + \gamma Z}{y_t} . \tag{7}$$

3.2.1 The Ideal Case with No Friction Losses

In this case the friction coefficient $C_f = 0$, and Equation (7) becomes:

$$\frac{(1 - Z)}{Z\left(1 + \frac{\gamma - 1}{2} Z\right)} \cdot \frac{dZ}{dy_t} + 2 \frac{d \ln A}{dy_t} = \frac{1 + \gamma Z}{y_t} . \tag{8}$$

and the constant Mach number area variation is given by:

$$Rel\ (A) = [y_t]^{\frac{1+\gamma 2}{2}} , \tag{9}$$

Equation (8) in conjunction with Equation (5) gives:

$$\frac{(1 - Z)}{Z\left(1 + \frac{\gamma - 1}{2} Z\right)} dZ = [(1 - 2m) + \gamma Z] \cdot \frac{dy_t}{y_t} . \tag{10}$$

$$\text{By putting } \alpha_0 = \frac{\gamma}{1 - 2m} \tag{11}$$

and integrating Equation (10) we finally obtain

$$Rel\left\{\frac{Z}{1 + \frac{\gamma - 1}{2} Z}\right\} \cdot Rel\left\{\frac{1 + \alpha_0 Z}{1 + \frac{\gamma - 1}{2} Z}\right\}^{\left(\frac{1 + \alpha_0}{\frac{\gamma - 1}{2} - \alpha_0}\right)} = y_t^{(1-2m)} . \tag{12}$$

In the case of a cylindrical duct $m = 0$ and Equation (12) becomes:

$$Rel \frac{Z\left(1 + \frac{\gamma - 1}{2} Z\right)}{(1 + \gamma Z)^2} = y_t . \tag{13}$$

3.2.2 The General Case

In the general case the same formulae are valid, with the difference that we use α instead of α_0.

$$\alpha = \frac{\gamma}{1 - 2m}\left(1 + \frac{2m \cdot C_f}{\sin 2\theta}\right). \tag{14}$$

In the case of a cylindrical duct $m = 0$, and Equation (14) becomes indefinite, by modifying it as follows:

$$\frac{2m}{\sin 2\theta} = \frac{1}{\cos^2 \theta} \cdot \frac{2y_t}{r} \cdot \frac{dx}{dy_t} \tag{15}$$

we obtain:

$$\alpha^* = \gamma\left(1 + \frac{2y_t}{R} \cdot \frac{dx}{dy_t} \cdot C_f\right). \tag{16}$$

Calling

$$\omega = \frac{2\gamma}{\gamma + 1} \cdot \frac{y_t}{R} \cdot \frac{dx}{dy_t} \cdot C_f \tag{17}$$

we transform Equation (12) as follows:

$$y_t = Rel\left[\frac{Z\left(1 + \frac{\gamma - 1}{2} Z\right)}{(1 + \gamma Z)^2}\right] \cdot Rel\left[\frac{1 + \frac{\gamma - 1}{2} Z}{1 + [\gamma + (\gamma + 1)\omega]\, Z}\right]^{\frac{(2 + 2\omega)}{(1 + 2\omega)}} \cdot Rel\left[\frac{(1 + \gamma Z)}{1 + \frac{\gamma - 1}{2} Z}\right]^2. \tag{18}$$

If moderate losses are assumed then $\omega \ll 1$, and Equation (18) is transformed into:

$$Rel\left[\frac{Z\left(1 + \frac{\gamma - 1}{2} Z\right)}{(1 + \gamma Z)^2}\right] = y_t \cdot \left\{1 + 2(\gamma + 1)\left[\frac{Z_2}{1 + \gamma Z_2} - \frac{Z_1}{1 + \gamma Z_1}\right]\right\}. \tag{19}$$

From Equations (13) and (19) it can be ascertained that the friction losses are equivalent to a convergence effect on the flow. We see from Equation (10) that an extreme value of y_t is obtained when $M = 1$, i.e., choking occurs.

3.3.0 The Total Head Pressure Ratio

From Equations (1) and (2) we obtain the following:

$$d\left\{p_t \frac{1 + \gamma Z}{\left[1 + \frac{\gamma - 1}{2} Z\right]^{\frac{\gamma}{\gamma - 1}}} A\right\} - \left\{\frac{p_t}{\left[1 + \frac{\gamma - 1}{2} Z\right]^{\frac{\gamma}{\gamma - 1}}} - \frac{C_f}{\sin 2\theta} \cdot \frac{\gamma p_t Z}{\left[1 + \frac{\gamma - 1}{2} Z\right]^{\frac{\gamma}{\gamma - 1}}}\right\} dA = 0, \tag{20}$$

and finally after some simple calculations as shown in Appendix II we obtain:

$$Rel\ p_t = Rel \left\{ \frac{\left[1 + \frac{\gamma - 1}{2} Z\right]^{\alpha\left(\frac{\gamma+1}{\gamma-1}\right)}}{[(1 + \alpha Z)]^{(1+\alpha)}} \right\}^{\frac{1}{2\alpha+1-\gamma}} . \tag{21}$$

From Equation (21) it is seen that if α is constant no pressure loss will occur if the Mach number is kept constant along the duct. From Equations (5) and (7) this will correspond to:

$$m = \frac{1 + \gamma Z}{2\left(1 - \frac{\gamma C_f Z}{\sin 2\theta}\right)} , \tag{22}$$

where a mean value of $\frac{C_f}{\sin 2\theta}$ is to be taken. Substituting this in Equation (14) we obtain the following:

$$\alpha' = -\frac{1}{Z} . \tag{23}$$

3.4.0 The Static Temperature Ratio

The static temperature is found to be:

$$y_s = \frac{y_t}{Rel\left(1 + \frac{\gamma - 1}{2} Z\right)} , \tag{24}$$

and using Equation (12) we obtain:

$$y_s^{(1-2m)} = \frac{Rel\left[\frac{Z}{1 + \frac{\gamma - 1}{2} Z}\right]}{Rel\left[1 + \frac{\gamma - 1}{2} Z\right]^{(1-2m)} . Rel\left[\frac{1 + \gamma Z}{1 + \frac{\gamma - 1}{2} Z}\right]^{\left(\frac{1+\alpha}{\alpha - \frac{\gamma-1}{2}}\right)}} . \tag{25}$$

For an extreme value of y_s we differentiate and finally obtain:

$$Z_{ex}^2 \alpha(1 - 2m) - 2Z_{ex}\left[m - \frac{\gamma + 1}{2(\gamma - 1)}\right] - \frac{2}{\gamma - 1} = 0 . \tag{26}$$

Solving Equation (26) we obtain

$$Z_{ex} = \frac{\left[m - \frac{\gamma + 1}{2(\gamma - 1)}\right] \pm \sqrt{\left[m - \frac{\gamma + 1}{2(\gamma - 1)}\right]^2 + \frac{2\alpha(1 - 2m)}{\gamma - 1}}}{\alpha(1 - 2m)} . \tag{27}$$

Only the positive root has a physical meaning.

3.5.0 The Static Pressure Ratio

The static pressure ratio is given by

$$Rel\ p_s = \frac{Rel\ p_t}{Rel\left[1 + \frac{\gamma - 1}{2} Z\right]^{\left(\frac{\gamma}{\gamma-1}\right)}} , \tag{28}$$

and using Equation (21) we obtain:

$$Rel\ p_s = Rel \frac{\left[1 + \frac{\gamma - 1}{2} Z\right]^{\left(\frac{\gamma - \alpha}{2\left(\alpha - \frac{\gamma - 1}{2}\right)}\right)}}{\left[(1 + \alpha Z)\right]^{\left(\frac{(1+\alpha)}{2\left(\alpha - \frac{\gamma - 1}{2}\right)}\right)}} . \tag{29}$$

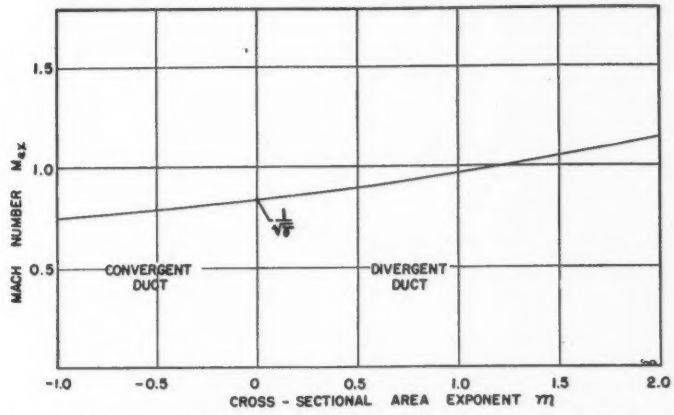

FIG. 2. *Variation of the extreme Mach number with the cross-sectional exponent.*

4.0 Results and Discussion

Fig. 2 shows the different values of the Mach number at which the static temperature reaches an extreme value, as a function of the exponent m associated with the cross-section. This holds in the absence of friction losses; when there are friction losses the small divergence effect of friction may be easily accounted for.

From Fig. 2 it is seen that M_{ex} increases continuously with increasing m. Thus for a cylindrical duct $m = 0$, $M_{ex} = \frac{1}{\sqrt{\gamma}}$, and for a divergent one for which $m = 1.2$, $M_{ex} = 1.0$.

Figs. 3, 5, 7, and 9 show the variation of the total head and static temperature ratios as a function of the Mach number for given exponents of the cross-section $m = 0, 0.5, 1.0$, and 1.5 respectively.

Figs. 4, 6, 8, and 10 show the variation of the total head and static pressure ratios as a function of the Mach number and the same exponents m.

From an inspection of the above curves, it can be seen that in a duct considerable amounts of heat may be added with small total head pressure loss if the duct is divergent enough and no increase in Mach number occurs.

In the subsonic region if the divergence is small (m small) addition of heat in the stream is followed by a simultaneous acceleration of the fluid and increase of the Mach number; on the other hand, if the divergence is large, heat may be

added in the stream, and this is followed by a simultaneous decrease of the Mach number.

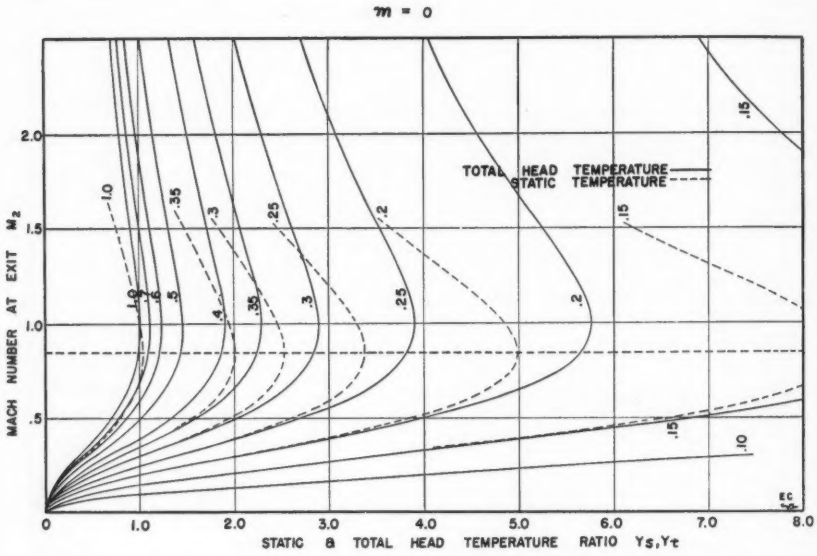

FIG. 3. *Variation of the static and total head temperature ratio with the Mach number.*

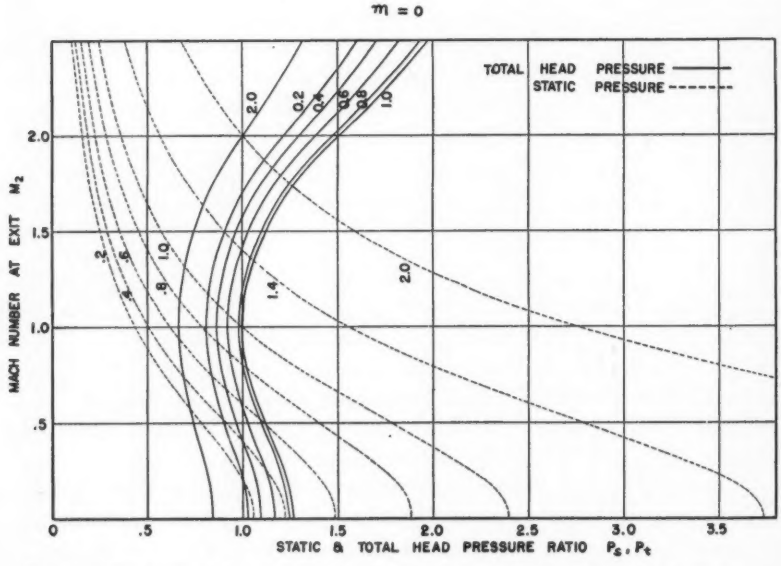

FIG. 4. *Variation of the static and total head pressure ratio with the Mach number.*

In the supersonic region, addition of heat in the stream is followed by a decrease of the Mach number, except when the relative divergence of the duct is very large and the initial Mach number approaches unity.

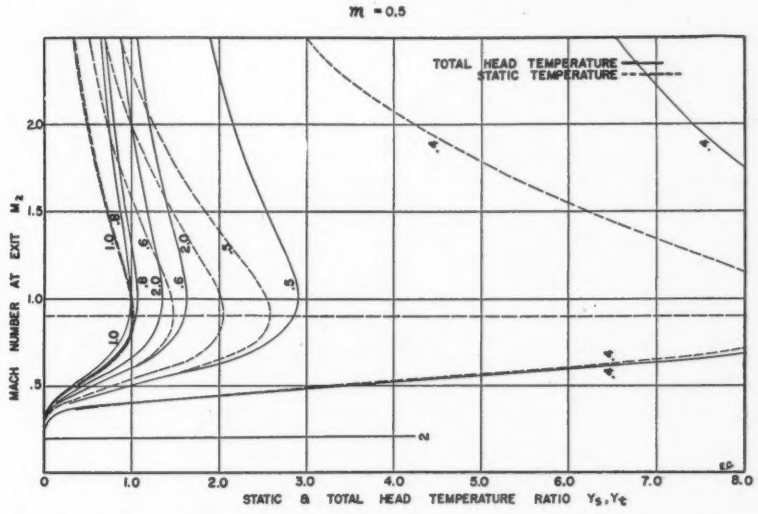

FIG. 5. *Variation of the static and total head temperature ratio with the Mach number.*

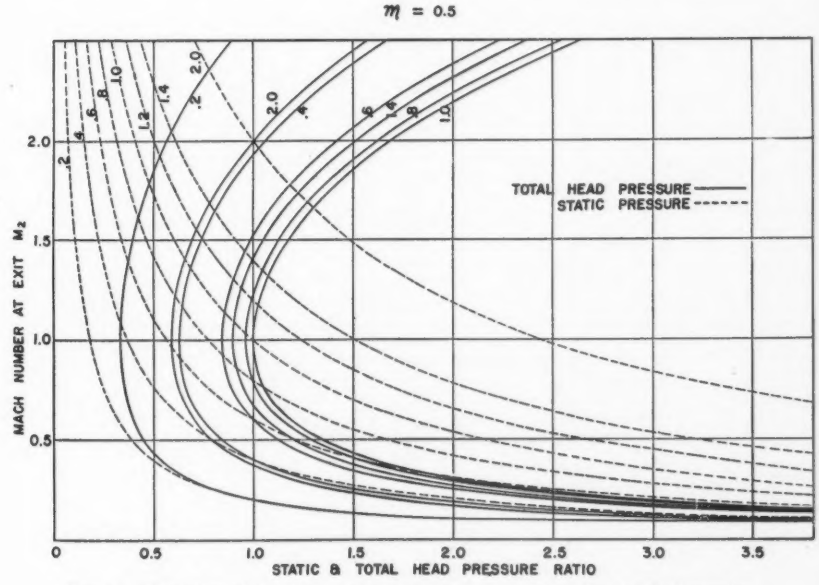

FIG. 6. *Variation of the static and total head pressure ratio with the Mach number.*

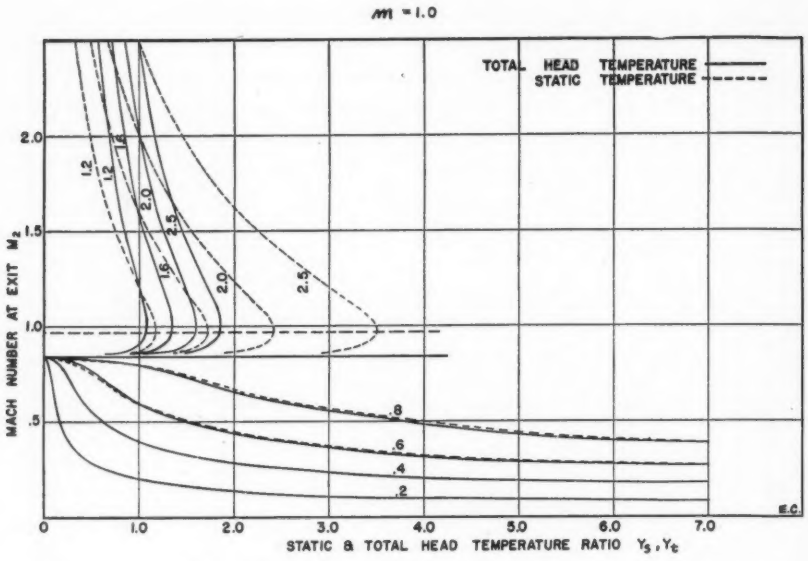

FIG. 7. *Variation of the static and total head temperature ratio with the Mach number.*

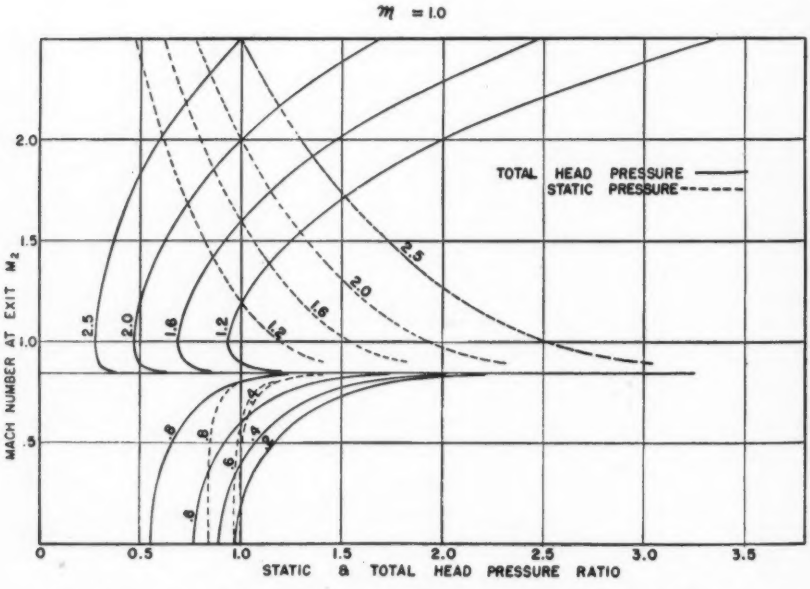

FIG. 8. *Variation of the static and total head pressure ratio with the Mach number.*

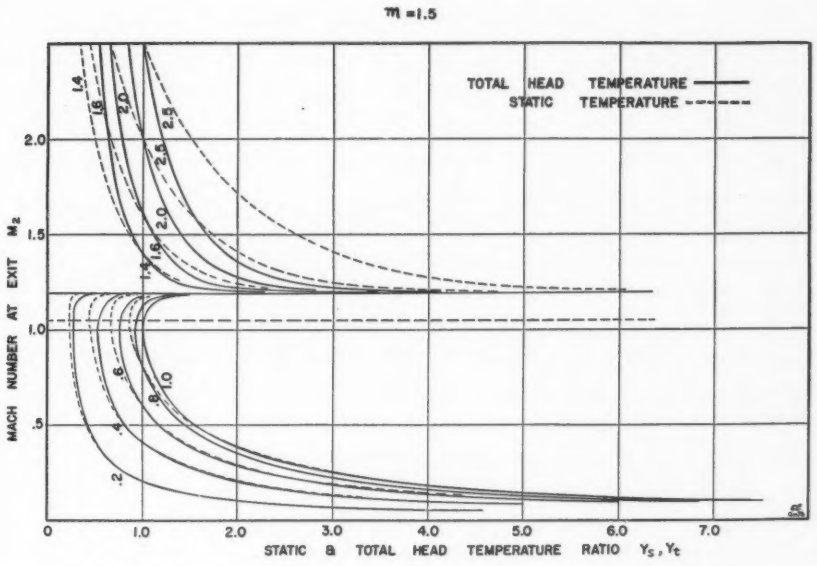

FIG. 9. *Variation of the static and total head temperature ratio with the Mach number.*

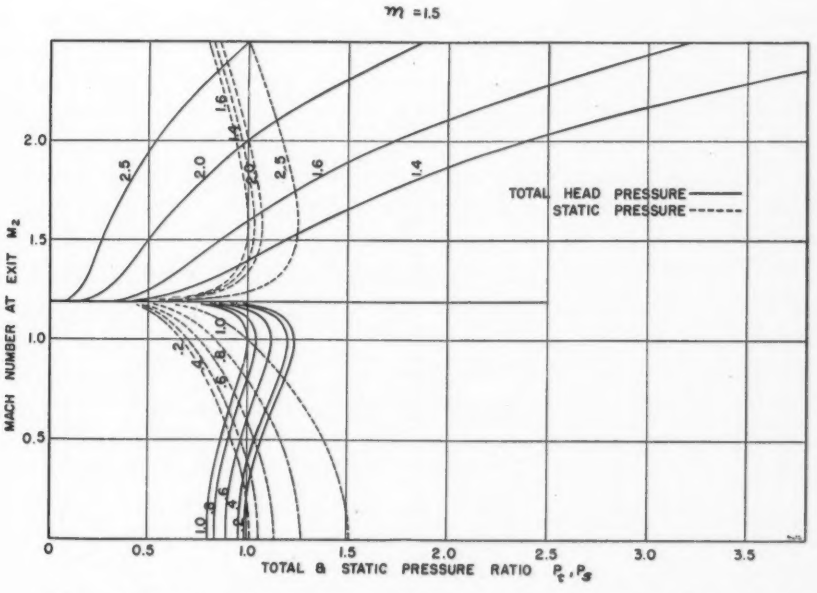

FIG. 10. *Variation of the static and total head pressure ratio with the Mach number.*

When $m < \frac{1+\gamma}{2}$ the maximum total head pressure loss occurs always when the Mach number equals unity. In the subsonic region the relative value increases with decreasing inlet Mach number, although in the supersonic region the opposite is true.

When $m > \frac{1+\gamma}{2}$ instead of total head pressure loss a total head pressure gain occurs and the maximum occurs when the Mach number equals unity; the reason for this is that the total head temperature decreases as the Mach number increases; therefore heat addition takes place only when the Mach number decreases.

5.0 Conclusions

From the above analysis and discussion it may be concluded that:

Heat can be added in a duct until the Mach number at a certain cross-section, most often the outlet, reaches unity.

In a duct, the total head temperature and pressure ratio reach an extreme value when the Mach number equals unity.

In the subsonic region the larger the divergence of the duct and the smaller the inlet Mach number, the larger is the extreme value of the total head temperature, i.e., the larger the amount of the heat acquired by the fluid.

In the supersonic region the larger the divergence of the duct and the larger the inlet Mach number, the larger is the extreme value of the total head temperature.

The static temperature reaches an extreme value for several values of the Mach number, smaller or larger than unity, depending on the divergence of the duct; but the static temperature does not represent the amount of the heat added in the fluid.

The friction losses result in a convergence effect on the duct. In the ideal case of a divergent duct with no friction losses, heat can be added without total head pressure loss if the Mach number is kept constant. In the real case a larger divergence must be used in order to compensate for the convergence effect of friction.

Appendix I

Derivation of the Mach Number Equation

From Equation (1), by substitution Equation (6) was found:

$$d\left\{\rho_s V^2 A\left(1+\frac{1}{\gamma Z}\right)\right\} - p_s dA + \tfrac{1}{2} C_f \rho_s \left(\frac{V}{\cos\theta}\right)^2 . 2\pi r dx = 0, \qquad (6)$$

and from Equations (3) and (4)

$$Vd\left\{\frac{V}{g} Q\left(1+\frac{1}{\gamma Z}\right) - \frac{VR_c T_t}{1+\frac{\gamma-1}{2}Z} \cdot g\rho_s dA + \frac{\rho_s V}{2} C_f \left(\frac{V}{\cos\theta}\right)^2 2\pi r dr = 0,\right.$$

and substituting for $dA = 2\pi r dr$, $dr = dx \cdot tg\theta$ and differentiating:

$$V^2 d\left(\frac{1}{\gamma Z}\right) + \left(1 + \frac{1}{\gamma Z}\right)\frac{1}{2} dV^2 - g\frac{\rho_s V}{Q} \cdot \frac{gR_c T_t dA}{1 + \frac{\gamma - 1}{2} Z} + \frac{g\rho_s V}{Q} C_f \frac{V^2 dA}{\sin 2\theta} = 0,$$

and

$$-g\gamma R_c \frac{Z \cdot y_t dZ}{\gamma Z^2\left(1 + \frac{\gamma - 1}{2} Z\right)} + \frac{1}{2}\left(1 + \frac{1}{\gamma Z}\right) d\left\{\frac{Z y_t}{1 + \frac{\gamma - 1}{2} Z}\right\} g\gamma R_c$$

$$- g\gamma R_c \left\{\frac{y_t}{\gamma\left(1 + \frac{\gamma - 1}{2} Z\right)} - \frac{C_f}{\sin 2\theta} \frac{Z y_t}{\left(1 + \frac{\gamma - 1}{2} Z\right)}\right\} \frac{dA}{A} = 0$$

$$- \frac{y_t dZ}{\gamma Z\left(1 + \frac{\gamma - 1}{2} Z\right)} + \frac{1}{2} \frac{1 + \gamma Z}{\gamma\left(1 + \frac{\gamma - 1}{2} Z\right)} dy_t + \frac{1}{2} \frac{1 + \gamma Z}{\gamma Z}$$

$$\cdot y_t \frac{dZ}{\left(1 + \frac{\gamma - 1}{2} Z\right)^2} - y_t \frac{d \ln A}{\gamma\left(1 + \frac{\gamma - 1}{2} Z\right)} \left(1 - \frac{\gamma Z C_f}{\sin 2\theta}\right) = 0$$

$$- \frac{y_t}{Z} \cdot \frac{dZ}{dy_t} + \frac{1}{2}(1 + \gamma Z) + \frac{y_t(1 + \gamma Z)}{2Z\left(1 + \frac{\gamma - 1}{2} Z\right)} \cdot \frac{dZ}{dy_t}$$

$$- y_t\left(1 - \frac{\gamma Z C_f}{\sin 2\theta}\right) \frac{d(\ln A)}{dy_t} = 0$$

and finally

$$\frac{1 - Z}{Z\left(1 + \frac{\gamma - 1}{2} Z\right)} \cdot \frac{dZ}{dy_t} + 2\left(1 - \frac{\gamma C_f Z}{\sin 2\theta}\right) \cdot \frac{d(\ln A)}{dy_t} = \frac{1 + \gamma Z}{y_t}. \quad (7)$$

Appendix II

Derivation of the Total Head Pressure Ratio Equation

From Equations (1) and (2) we obtain the following:

$$d\left\{\frac{p_t(1 + \gamma Z)A}{\left(1 + \frac{\gamma - 1}{2} Z\right)^{\left(\frac{\gamma}{\gamma - 1}\right)}}\right\} - \frac{p_t dA}{\left(1 + \frac{\gamma - 1}{2} Z\right)^{\left(\frac{\gamma}{\gamma - 1}\right)}} +$$

$$\frac{C_f}{\sin 2\theta} \cdot \frac{\gamma p_t Z dA}{\left(1 + \frac{\gamma - 1}{2} Z\right)^{\left(\frac{\gamma}{\gamma - 1}\right)}} = 0,$$

and

$$\frac{p_t(1+\gamma Z)}{\left(1+\frac{\gamma-1}{2}Z\right)^{\left(\frac{\gamma}{\gamma-1}\right)}}+\frac{d}{d(\ln A)}\left\{\frac{p_t(1+\gamma Z)}{\left(1+\frac{\gamma-1}{2}Z\right)^{\left(\frac{\gamma}{\gamma-1}\right)}}\right\}$$

$$-\frac{p_t}{\left(1+\frac{\gamma-1}{2}Z\right)^{\left(\frac{\gamma}{\gamma-1}\right)}}+\frac{C_f}{\sin 2\theta}\frac{\gamma p_t Z}{\left(1+\frac{\gamma-1}{2}Z\right)^{\left(\frac{\gamma}{\gamma-1}\right)}}=0,$$

and

$$\gamma p_t Z\frac{1+\frac{C_f}{\sin 2\theta}}{\left(1+\frac{\gamma-1}{2}Z\right)^{\left(\frac{\gamma}{\gamma-1}\right)}}+\frac{d}{d(\ln A)}\left\{\frac{p_t(1+\gamma Z)}{\left(1+\frac{\gamma-1}{2}Z\right)^{\left(\frac{\gamma}{\gamma-1}\right)}}\right\}=0,$$

but

$$d(\ln A)=m\frac{dy_t}{y_t}=\frac{m}{1-2m}\cdot\frac{(1-Z)dZ}{Z\left(1+\frac{\gamma-1}{2}Z\right)(1+\alpha Z)},$$

and substituting in the former equation we obtain:

$$\frac{\gamma m}{1-2m}\left(1+\frac{C_f}{\sin 2\theta}\right)\frac{(1-Z)dZ}{(1+\alpha Z)(1+\gamma Z)\left(1+\frac{\gamma-1}{2}Z\right)}$$

$$+d\ln\left\{\frac{p_t(1+\gamma Z)}{\left(1+\frac{\gamma-1}{2}Z\right)^{\left(\frac{\gamma}{\gamma-1}\right)}}\right\}=0,$$

and after integration

$$Rel\left\{\frac{p_t(1+\gamma Z)}{\left(1+\frac{\gamma-1}{2}Z\right)^{\left(\frac{\gamma}{\gamma-1}\right)}}\right\}=Rel\left\{\frac{\left(1+\frac{\gamma-1}{2}Z\right)^{(\gamma-\alpha)}}{(1+\alpha Z)^{(1+\alpha)}(1+\gamma Z)^{(\gamma-1-2\alpha)}}\right\}^{\frac{\frac{m\gamma}{1-2m}\left(1+\frac{C_f}{\sin 2\theta}\right)}{(\gamma-\alpha)\left(\frac{\gamma-1}{2}-\alpha\right)}}$$

and after some algebraic transformations we finally obtain

$$Rel\ p_t=Rel\left\{\frac{\left(1+\frac{\gamma-1}{2}Z\right)^{\left(\frac{\gamma+1}{\gamma-1}\alpha\right)}}{(1+\alpha Z)^{(1+\alpha)}}\right\}^{\left(\frac{1}{2\alpha+1-\gamma}\right)}. \qquad (21)$$